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Supporting Information

for

Photoredox-catalyzed silyldifluoromethylation of silyl enol ethers

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Full experimental details, compound characterization, and copies of NMR spectra

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General Methods. Dichloromethane was distilled from CaH_2. Column chromatography was carried out employing silica gel (230–400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage –4500 V) or in a negative ion mode (3200 V); mass range from *m*/*z* 50 to *m*/*z* 3000.

Reagents. Silyl enol ethers **2** were prepared according to a literature procedure and distilled under vacuum.[1] (Bromodifluoromethyl)trimethylsilane (**1**)[2] and photocatalyst $[AuCl(\mu\text{-dppm})]_2$[3] were prepared according to literature procedures.

Reaction of silyl enol ethers with silane 1 (general procedure).

(a) A tube (Duran, Roth cat. no K248.1, outside diameter = 12 mm) containing a stirring bar was charged with $[AuCl(\mu\text{-dppm})]_2$ (1.5 mg, 0.0012 mmol, 0.25 mol %), and then was evacuated and filled with argon. Dichloromethane (2 mL), silyl enol ether **2** (0.50 mmol), and silane **1** (for **4a–n** and **3p**, 152 mg, 0.75 mmol, 1.5 equiv; for **4o**, 102 mg, 0.50 mmol, 1.0 equiv) were added. The tube was closed tightly with a screw-cap and placed in a water bath. The reaction mixture was stirred, and the tube was irradiated by a 375 nm LED chip operated at 18 watt, distance between LED chip and the reaction tube was 1 cm. Irradiation time: for **4a–e**,**g–j**,**l–o** and **3p**, 6 hours; for **4f**,**k**, 24 h. During the reaction, the bath temperature was maintained in a range of 13–15 °C.

(b) For **4a–p**, the mixture was poured into a 100 mL flask containing $NaBH_4$ (76 mg, 2.0 mmol, 4.0 equiv) and ethanol (3 mL) cooled with ice/water. The reaction tube was rinsed with additional ethanol (2 mL) which was also poured into the flask, and the mixture was stirred for one hour at 0 to 5 °C. For the work-up, hydrochloric acid (1 M, 1 mL) was added followed by water (10 mL). For **4l** the solution was neutralized with solid NaOH (230 mg). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (3 × 2 mL). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

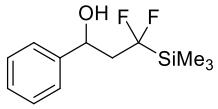
(c) For **3p**, water (10 mL) was added, the organic phase was separated, and the aqueous phase was extracted with dichloromethane (3 × 2 mL). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

[1] Scherbinina, S. I.; Fedorov, O. V.; Levin, V. V.; Kokorekin, V. A.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2017,** *82*, 12967–12974.

[2] Kosobokov, M. D.; Dilman, A. D.; Levin, V. V.; Struchkova, M. I. *J. Org. Chem.* **2012,** *77*, 5850–5855.

[3] Massai, L.; Fernández-Gallardo, J.; Guerri, A.; Arcangeli, A.; Pillozzi, S.; Contel, M.; Messori, L. *Dalton Trans.* **2015,** *44*, 11067–11076.

3,3-Difluoro-1-phenyl-3-(trimethylsilyl)propan-1-ol (4a).



Yield 63 mg (52 %). Colorless oil.

Chromatography: hexanes/EtOAc, from 20/1 to 10/1. R_f 0.26 (hexanes/EtOAc, 20/1).

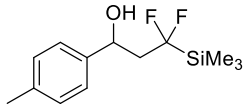
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 – 7.23 (m, 5H), 5.25 (d, *J* = 9.3 Hz, 1H), 2.50 (br s, 1H), 2.45 – 2.02 (m, 2H), 0.22 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 144.1, 130.8 (t, *J* = 259.1 Hz), 128.7, 127.8, 125.8, 68.7 (dd, *J* = 7.9 , 5.9 Hz), 45.4 (dd, *J* = 19.4, 18.1 Hz), -4.5 (t, *J* = 2.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.7 (ddd, *J* = 315.7, 31.3, 11.0 Hz, 1F), -115.0 (dddd, *J* = 315.7, 33.9, 12.8, 3.5 Hz, 1F).

HRMS (ESI): calcd for $C_{12}H_{22}F_2NO_2Si$ (M+NH_4) 262.1433, found 262.1434.

3,3-Difluoro-1-(*p*-tolyl)-3-(trimethylsilyl)propan-1-ol (4b).



Yield 80 mg (62 %). Yellow oil.

Chromatography: hexanes/EtOAc, from 7/1 to 5/1. R_f 0.22 (hexanes/EtOAc, 7/1).

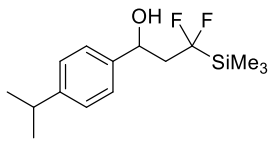
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.23 (d, *J* = 9.3 Hz, 1H), 2.48 (br s, 1H), 2.39 (s, 3H), 2.44-2.03 (m, 2H), 0.24 (s, 9H)

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 141.2, 137.4, 130.8 (t, *J* = 258.8 Hz), 129.3, 125.7, 68.5 (dd, *J* = 8.0, 5.9 Hz), 45.3 (dd, *J* = 19.3, 18.3 Hz), 21.2, -4.5 (t, *J* = 2.3 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.5 (ddd, *J* = 315.4, 29.3, 13.3 Hz, 1F), -115.2 (dddd, *J* = 315.4, 31.6, 13.7, 4.9 Hz, 1F)

HRMS (ESI): calcd for $C_{13}H_{20}F_2NaOSi$ (M+Na) 281.1144, found 281.1155.

3,3-Difluoro-1-(4-isopropylphenyl)-3-(trimethylsilyl)propan-1-ol (4c).



Yield 85 mg (59 %). Colorless oil.

Chromatography: hexanes/EtOAc, 10/1. R_f 0.28 (hexanes/EtOAc, 10/1).

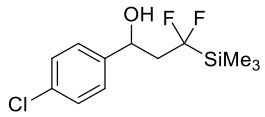
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 9.2 Hz, 1H), 2.96 (sept, *J* = 7.0 Hz, 1H), 2.50 (br d, *J* = 5.3 Hz, 1H), 2.46 – 2.05 (m, 2H), 1.31 (d, *J* = 7.0 Hz, 6H), 0.25 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 148.4, 141.5, 130.8 (dd, *J* = 259.6, 258.2 Hz), 126.7, 125.8, 68.5 (dd, *J* = 8.1, 5.9 Hz), 45.2 (dd, *J* = 19.3,18.2 Hz), 33.9, 24.1, -4.2 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.5 (ddd, *J* = 315.4, 29.0, 13.4 Hz, 1F), -115.1 (dddd, *J* = 315.4, 31.6, 13.9, 5.3 Hz, 1F).

HRMS (ESI): calcd for $C_{15}H_{24}F_2NaOSi$ (M+Na) 309.1457, found 309.1459.

1-(4-Chlorophenyl)-3,3-difluoro-3-(trimethylsilyl)propan-1-ol (4d).



Yield 80 mg (57 %). Yellowish crystals. Mp 43 – 44 °C.

Chromatography: hexanes/EtOAc, 10/1. R_f 0.28 (hexanes/EtOAc, 10/1).

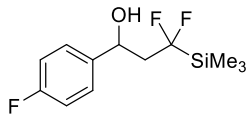
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.34 (m, 4H), 5.24 (d, *J* = 9.1 Hz, 1H), 2.59 (br d, *J* = 4.9 Hz, 1H), 2.42-1.96 (m, 2H), 0.22 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 142.5, 133.4, 130.7 (t, *J* = 258 .3 Hz), 128.8, 127.2, 68.0 (dd, *J* = 7.9, 5.8 Hz), 45.2 (dd, *J* = 19.6, 18.1 Hz), -4.6 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -114.1 (ddd, *J* = 315.4, 30.2, 12.4 Hz, 1F), -115.9 (dddd, *J* = 315.4, 31.8, 11.1, 4.9 Hz).

HRMS (ESI): calcd for $C_{12}H_{17}F_5{}^{35}ClNaOSi$ (M+Na) 301.0597, found 301.0599, $C_{12}H_{17}F_5{}^{37}ClNaOSi$ (M+Na) 303.0569, found 303.0569.

3,3-Difluoro-1-(4-fluorophenyl)-3-(trimethylsilyl)propan-1-ol (4e).



Yield 87 mg (66 %). Yellow oil.

Chromatography: hexanes/EtOAc, 5/1. R_f 0.37 (hexanes/EtOAc, 5/1).

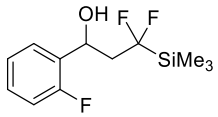
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.03 (dd, *J* = 8.7, 8.7 Hz, 2H), 5.22 (d, *J* = 8.9 Hz, 1H), 2.56 (br d, *J* = 4.4 Hz, 1H), 2.40-1.97 (m, 2H), 0.20 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 162.3 (d, *J* = 245.5 Hz), 139.8 (d, *J* = 3.2 Hz), 130.7 (dd, *J* = 259.9, 258.0 Hz), 127.4 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21.4 Hz), 68.1 (dd, *J* = 7.9, 6.0 Hz), 45.3 (dd, *J* = 19.0, 17.7 Hz), -4.6 (d, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.8 (ddd, *J* = 315.4, 29.9, 12.9 Hz, 1F), -115.5 (dddd, *J* = 315.4, 31.9, 12.9, 4.4 Hz, 1F), -115.7 (tt, *J* = 8.7, 5.4 Hz, 1F).

HRMS (ESI): calcd for $C_{12}H_{17}F_3NaOSi$ (M+Na) 285.0893, found 285.0893.

3,3-Difluoro-1-(2-fluorophenyl)-3-(trimethylsilyl)propan-1-ol (4f).



Yield 69 mg (53 %). Yellow oil.

Chromatography: hexanes/EtOAc, 5/1. R_f 0.22 (hexanes/EtOAc, 5/1).

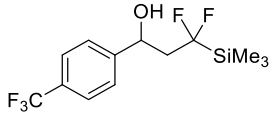
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58 (td, *J* = 7.6, 1.6 Hz, 1H), 7.33-7.25 (m, 1H), 7.19 (td, *J* = 7.6, 1.3 Hz, 1H), 7.05 (ddd, *J* = 10.6, 8.2, 1.2 Hz, 1H), 5.55 (d, *J* = 8.8 Hz, 1H), 2.60 (m, 1H), 2.43-2.11 (m, 2H), 0.24 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 159.5 (d, *J* = 245.7 Hz), 130.9 (d, *J* = 13.0 Hz), 130.8 (dd, J = 259.7, 258.4 Hz), 129.1 (d, *J* = 8.2 Hz), 127.4 (d, *J* = 4.3 Hz), 124.5 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 21.5 Hz), 63.1 (ddd, *J* = 9.9, 6.9, 3.0 Hz), 43.9 (td, *J* = 18.8, 1.3 Hz), -4.6 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.7 (dddd, *J* = 314.7, 26.5, 16.7, 4.6 Hz, 1F), -114.5 (ddd, *J* = 314.7, 25.3, 18.5 Hz, 1F), -120.0 (m, 1F).

HRMS (ESI): calcd for $C_{12}H_{17}F_3NaOSi$ (M+Na) 285.0893, found 285.0891.

3,3-Difluoro-1-[4-(trifluoromethyl)phenyl]-3-(trimethylsilyl)propan-1-ol (4g).



Yield 44 mg (28 %). Colorless crystals. Mp 55 – 57 °C.

Chromatography: hexanes/EtOAc, 10/1. R_f 0.32 (hexanes/EtOAc, 10/1).

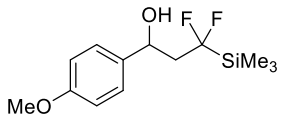
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 5.33 (d, *J* = 9.1 Hz, 1H), 2.63 (d, *J* = 6.3 Hz, 1H), 2.40 – 1.97 (m, 2H), 0.20 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 148.0, 130.7 (t, *J* = 257.6 Hz), 130.0 (q, *J* = 32.4 Hz), 126.2, 125.6 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.1 Hz), 68.2 (dd, *J* = 7.6, 5.9 Hz), 45.2 (dd, *J* = 19.3, 17.5 Hz), -4.7 (t, *J* = 2.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -63.3 (s, 3F), -114.1 (ddd, *J* = 315.4, 30.6, 12.4 Hz, 1F), -115.8 (dddd, *J* =315.4, 32.4, 11.6, 6.3 Hz, 1F).

HRMS (ESI): calcd for $C_{13}H_{17}F_5NaOSi$ (M+Na) 335.0861, found 335.0851.

3,3-Difluoro-1-(4-methoxyphenyl)-3-(trimethylsilyl)propan-1-ol (4h).



Yield 79 mg (58 %). Colorless oil.

Chromatography: hexanes/EtOAc, 4/1. R_f 0.35 (hexanes/EtOAc, 4/1).

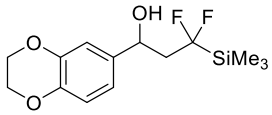
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.20 (d, *J* = 9.1 Hz, 1H), 3.83 (s, 3H), 2.48 (br d, *J* = 4.4 Hz 1H), 2.43 – 2.01 (m, 2H), 0.23 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 159.3, 136.4, 130.7 (t, *J* = 259.0 Hz), 127.0, 114.1, 68.3 (dd, *J* = 8.0, 5.9 Hz), 55.4, 45.3 (dd, *J* = 19.4, 18.2 Hz), -4.5 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.5 (ddd, *J* = 315.7, 28.9, 13.6 Hz, 1F), -115.0 (dddd, *J* = 315.7, 31.6, 13.9, 4.4 Hz, 1F).

HRMS (ESI): calcd for $C_{13}H_{20}F_2NaO_2Si$ (M+Na) 297.1093, found 297.1091.

1-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-3,3-difluoro-3-(trimethylsilyl)propan-1-ol (4i).



Yield 95 mg (63 %). Yellow oil. Chromatography: hexanes/EtOAc, 4/1. R_f 0.34 (hexanes/EtOAc, 4/1).

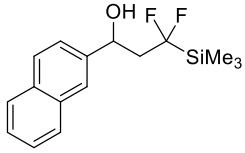
^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.90 (s, 1H), 6.84-6.81 (m, 2H), 5.09 (d, *J* = 9.1 Hz,1H), 4.23 (s, 4H), 2.48 (br s, 1H), 2.41-1.95 (m, 2H), 0.20 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 143.6, 143.1, 137.6, 130.6 (t, *J* = 258.8 Hz), 118.7, 117.3, 114.7, 68.2 (dd, *J* = 8.1, 5.8 Hz), 64.44, 64.42, 45.2 (dd, *J* = 19.3, 18.1 Hz), -4.5 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.4 (ddd, *J* = 315.7, 29.1, 13.4 Hz, 1F), -115.2 (dddd, *J* = 315.7, 45.2, 13.8, 4.0 Hz, 1F).

HRMS (ESI): calcd for $C_{14}H_{20}F_2NaO_3Si$ (M+Na) 325.1042, found 325.1034.

3,3-Difluoro-1-(naphthalen-2-yl)-3-(trimethylsilyl)propan-1-ol (4j).



Yield 91 mg (62 %). Yellow oil.

Chromatography: hexanes/EtOAc, 10/1. R_f 0.28 (hexanes/EtOAc, 10/1).

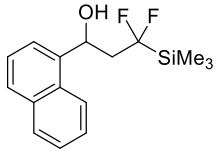
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.90 – 7.82 (m, 4H), 7.54 – 7.48 (m, 3H), 5.44 (d, *J* = 9.0 Hz, 1H), 2.67 (br d, *J* = 5.0 Hz, 1H), 2.54-2.12 (m, 2H), 0.25 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 141.4, 133.5, 133.1, 130.8 (t, *J* = 258.6), 128.5, 128.1, 127.8, 126.3, 126.0, 124.4, 123.9, 68.8 (dd, *J* = 8.0, 5.8 Hz), 45.3 (dd, *J* = 19.4, 18.2 Hz), -4.5 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.3 (ddd, *J* = 315.2, 29.6, 12.7 Hz, 1F), -115.2 (dddd, *J* = 315.2, 32.0, 13.2, 5.0 Hz, 1F).

HRMS (ESI): calcd for $C_{16}H_{20}F_2NaOSi$ (M+Na) 317.1144, found 317.1136.

3,3-Difluoro-1-(naphthalen-1-yl)-3-(trimethylsilyl)propan-1-ol (4k).



Yield 38 mg (26 %). Yellow oil.

Chromatography: hexanes/EtOAc, 10/1. R_f 0.26 (hexanes/EtOAc, 10/1).

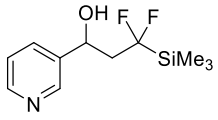
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.61-7.50 (m, 3H), 6.11 (d, *J* = 8.2 Hz, 1H), 2.66 (dd, *J* = 6.4, 2.1 Hz, 1H), 2.48 – 2.29 (m, 2H), 0.24 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 139.5, 133.9, 131.2 (dd, *J* = 259.3, 258.0 Hz), 129.9, 129.1, 128.2, 126.4, 125.68, 125.70, 122.8, 122.8, 65.2 (dd, *J* = 8.6, 5.2 Hz), 44.7 (dd, *J* = 19.4, 18.0 Hz), -4.5 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.8 (ddd, *J* = 314.9, 29.5, 13.4 Hz, 1F), -116.2 (dddd, *J* = 314.9, 31.8, 14.7, 6.4 Hz, 1F).

HRMS (ESI): calcd for $C_{16}H_{20}F_2NaOSi$ (M+Na) 317.1144, found 317.1141.

3,3-Difluoro-1-(pyridin-3-yl)-3-(trimethylsilyl)propan-1-ol (4l).



Yield 55 mg (45 %). Yellow oil.

Chromatography: EtOAc. R_f 0.30 (EtOAc).

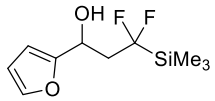
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 2.2 Hz, 1H), 8.40 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.74 (ddd, *J* = 8.0, 2.2, 1.7 Hz, 1H), 7.26 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.23 (dd, *J* = 8.7, 3.2 Hz, 1H), 4.03 (br s, 1H), 2.45 – 1.99 (m, 2H), 0.19 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 148.6, 147.5, 140.0, 133.8, 130.3 (t, *J* = 258.7 Hz), 123.6, 66.3 (dd, *J* = 8.2, 5.9 Hz), 45.1 (dd, *J* = 19.6, 18.5 Hz), -4.6 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.2 (ddd, *J* = 316.3, 29.9, 11.7 Hz, 1F), -115.2 (ddd, *J* = 316.3, 32.2, 12.9 Hz, 1F).

HRMS (ESI): calcd for $C_{11}H_{18}F_2NOSi$ (M+H) 246.1120, found 246.1127.

3,3-Difluoro-1-(furan-2-yl)-3-(trimethylsilyl)propan-1-ol (4m).



Yield 81 mg (69 %). Yellow oil.

Chromatography: hexanes/EtOAc, 4/1. R_f 0.28 (hexanes/EtOAc, 4/1).

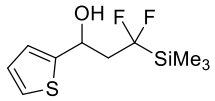
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.33 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.27 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.21 (d, *J* = 8.4 Hz, 1H), 2.52-2.20 (m, 3H), 0.20 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 155.8, 142.2, 130.3 (t, *J* = 259.2 Hz), 110.4, 106.1, 62.5 (dd, *J* = 8.6, 6.5 Hz), 41.5(dd, *J* = 19.5, 18.5 Hz), -4.6 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.4 (ddd, *J* = 316.6, 27.5, 14.3 Hz, 1F), -115.5 (dddd, *J* = 316.6, 29.8, 15.3, 3.6 Hz, 1F).

HRMS (ESI): calcd for $C_{10}H_{16}F_2NaO_2Si$ (M+Na) 257.0780, found 257.0784.

3,3-Difluoro-1-(thiophen-2-yl)-3-(trimethylsilyl)propan-1-ol (4n).



Yield 70 mg (56 %). Colorless oil.

Chromatography: hexanes/EtOAc, 6/1. R_f 0.34 (hexanes/EtOAc, 6/1).

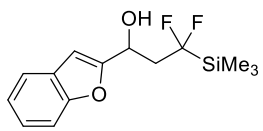
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.03 – 6.97 (m, 2H), 5.52 (d, *J* = 8.8 Hz, 1H), 2.65 (br s, 1H), 2.57 – 2.18 (m, 2H), 0.23 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 147.9, 130.4 (t, *J* = 258.8 Hz), 126.8, 124.7, 123.5, 65.0 (dd, *J* = 8.7, 6.2 Hz), 45.4 (dd, *J* = 19.3, 18.3 Hz), -4.6 (t, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.8 (ddd, *J* = 316.3, 25.3, 16.3 Hz, 1F), -115.2 (dddd, *J* = 316.3, 33.7, 12.8, 4.6 Hz, 1F).

HRMS (ESI): calcd for $C_{10}H_{16}F_2NaO_2SSi$ (M+Na) 273.0551, found 273.0548.

1-(Benzofuran-2-yl)-3,3-difluoro-3-(trimethylsilyl)propan-1-ol (4o).



Yield 53 mg (37 %). Yellow oil.

Chromatography: hexanes/EtOAc, from 10/1 to 5/1. R_f 0.35 (hexanes/EtOAc, 5/1).

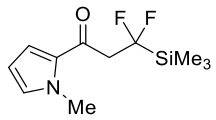
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.21 (m, 2H), 6.70 (s, 1H), 5.45-5.39 (m, 1H), 2.65 (br s, 1H), 2.58 – 2.39 (m, 2H), 0.26 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 158.4, 155.0, 130.4 (d, *J* = 259.6, 258.7 Hz), 128.2, 124.4, 123.0, 121.3, 111.4, 102.9, 63.2 (dd, *J* = 8.5, 6.8 Hz), 41.6 (t, *J* = 19.0 Hz), -4.6 (t, *J* = 2.3 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ: -114.0 (ddd, *J* = 315.7, 26.1, 15.9 Hz, 1F), -115.4 (dddd, *J* = 315.7, 27.2, 16.8, 4.5 Hz, 1F).

HRMS (ESI): calcd for $C_{14}H_{18}F_2NaO_2Si$ (M+Na) 307.0936, found 307.0932.

3,3-Difluoro-1-(1-methyl-1*H*-pyrrol-2-yl)-3-(trimethylsilyl)propan-1-one (3p).



Yield 39 mg (32 %). Yellow oil.

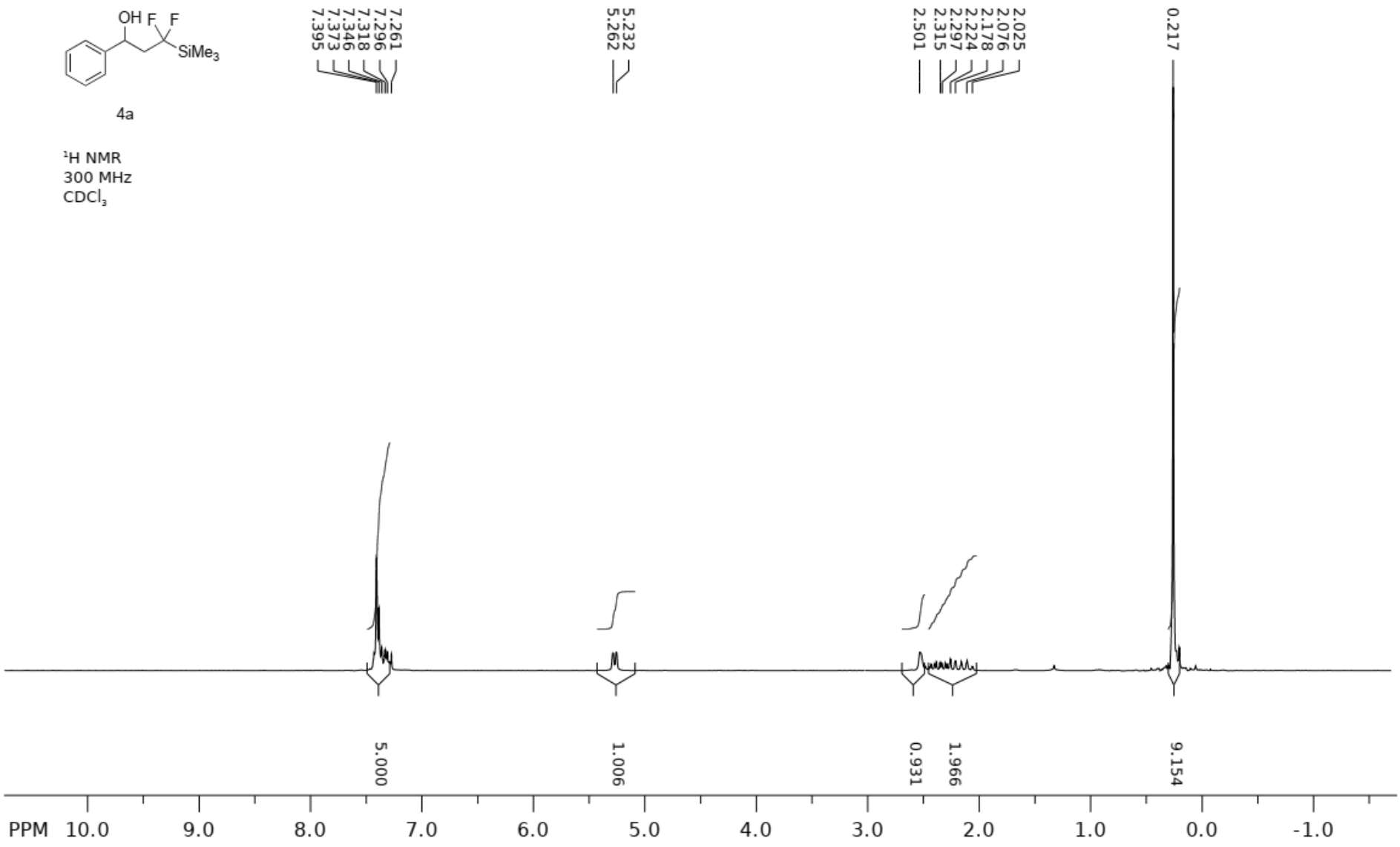
Chromatography: hexanes/EtOAc, from 7/1 to 5/1. R_f 0.21 (hexanes/EtOAc, 7/1).

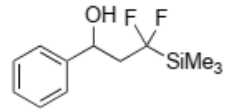
^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.98 (dd, *J* = 4.2, 1.5 Hz, 1H), 6.83 (dd, *J* = 2.5, 1.5 Hz, 1H), 6.14 (dd, *J* = 4.2, 2.5 Hz, 1H), 3.93 (s, 3H), 3.29 (t, *J* = 20.3 Hz, 2H), 0.21 (s, 9H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 184.4 (t, *J* = 7.4 Hz), 132.1, 128.5 (t, *J* = 261.9 Hz), 121.4, 108.4, 46.9 (t, *J* = 21.8 Hz), 37.9, -3.8 (t, *J* = 2.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -107.7 (t, *J* = 20.1 Hz).

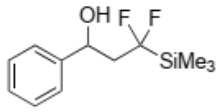
HRMS (ESI): calcd for $C_{11}H_{18}F_2NOSi$ (M+H) 246.1120, found 246.1125.


OH F F
SiMe3
4a
1H NMR
300 MHz
CDCl3
7.395
7.373
7.346
7.318
7.296
7.261
5.262
5.232
2.501
2.315
2.297
2.224
2.178
2.076
2.025
0.217
5.000
1.006
0.931
1.966
9.154
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0



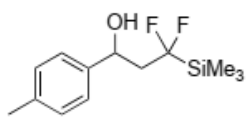
4a

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$



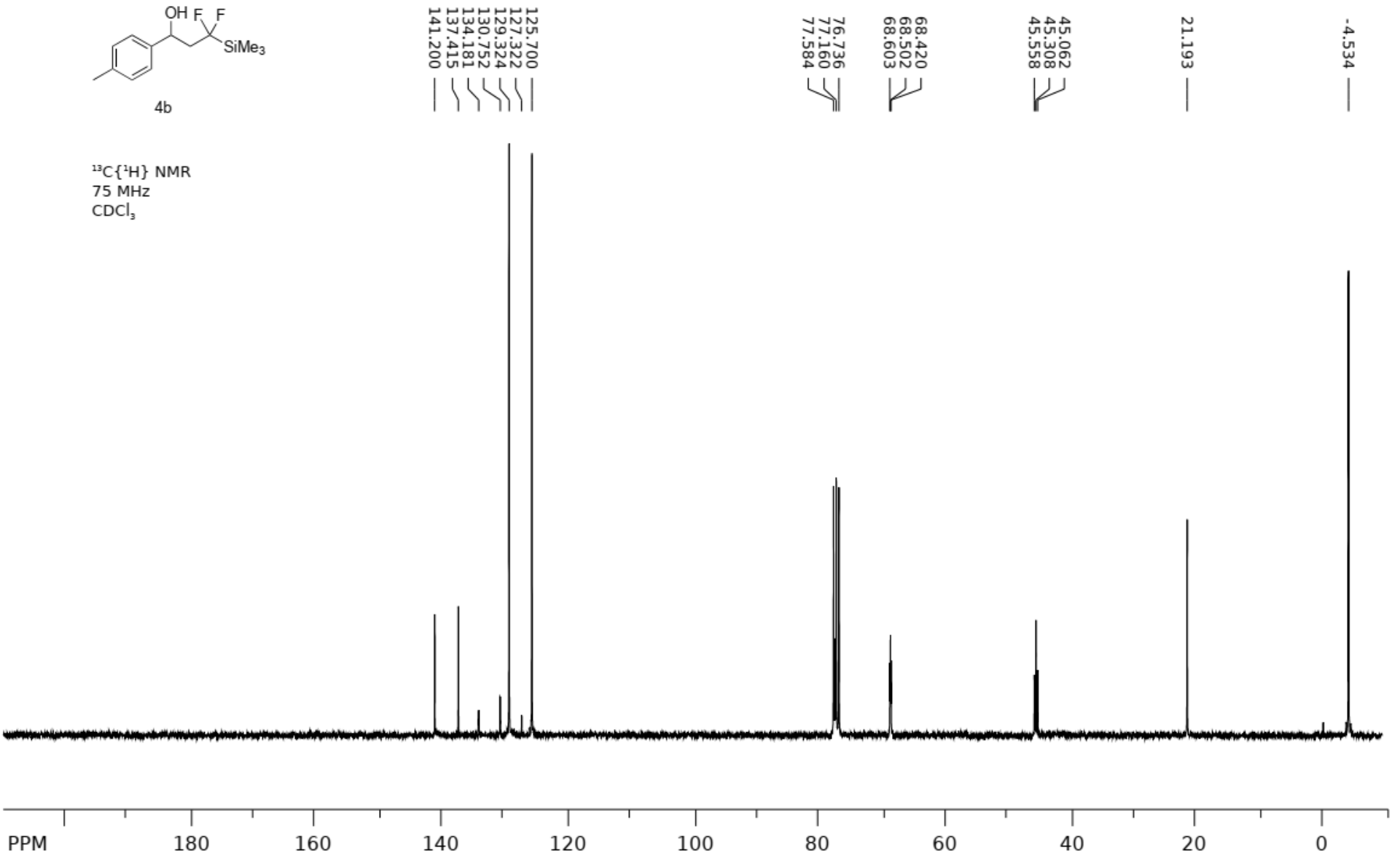
4a

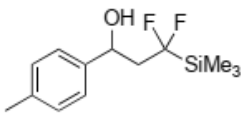
^{19}F NMR
282 MHz
$CDCl_3$



4b

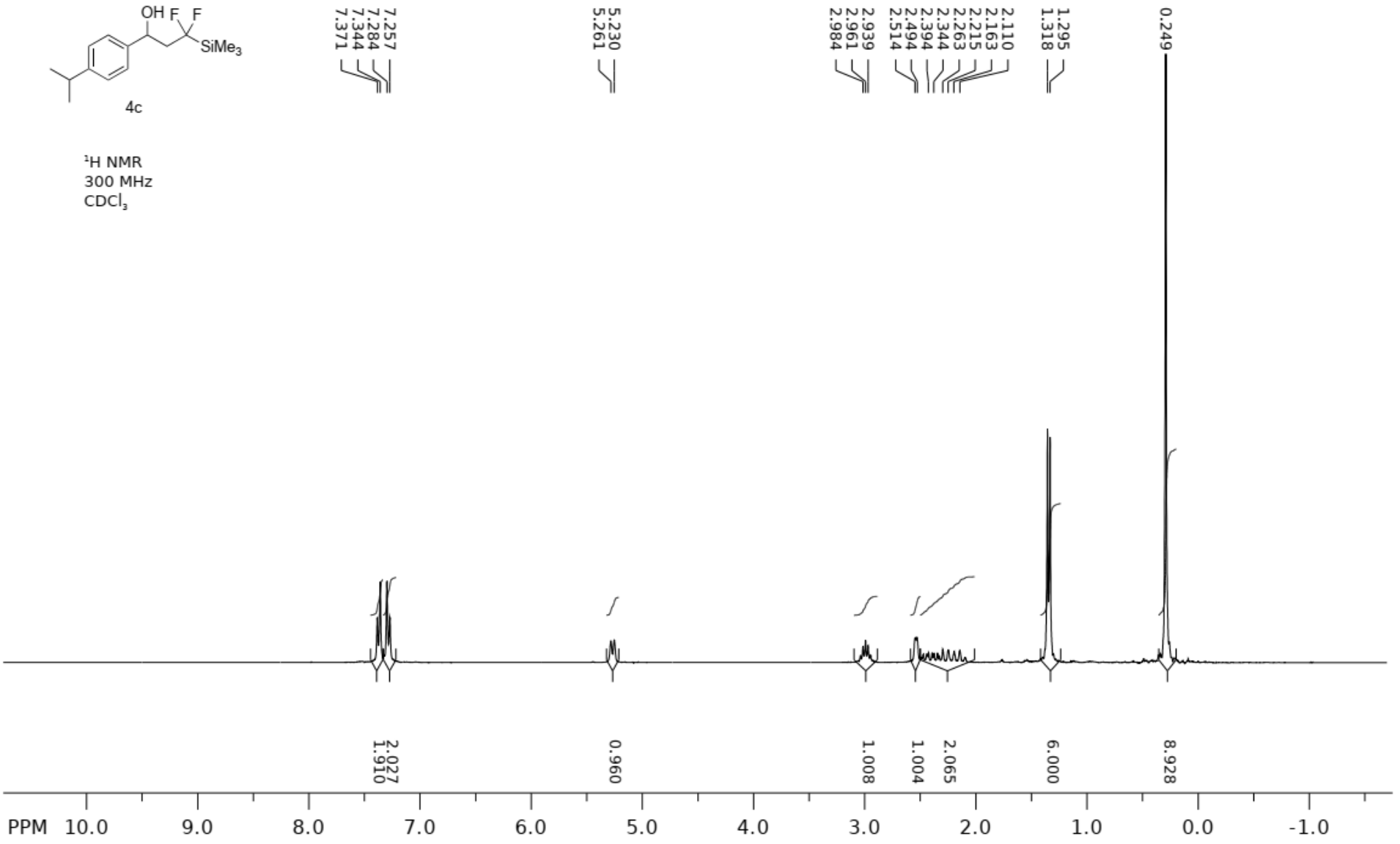
^{1}H NMR
300 MHz
$CDCl_3$

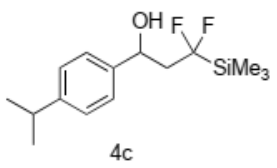

OH F F
SiMe3
4b
141.200
137.415
134.181
130.752
129.324
127.322
125.700
77.584
77.160
76.736
68.603
68.502
68.420
45.558
45.308
45.062
21.193
-4.534
13C{1H} NMR
75 MHz
CDCl3
PPM
180
160
140
120
100
80
60
40
20
0



4b

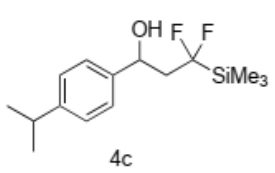
^{19}F NMR
282 MHz
$CDCl_3$


OH F F
SiMe3
4c
1H NMR
300 MHz
CDCl3
7.371
7.344
7.284
7.257
5.261
5.230
2.984
2.961
2.939
2.514
2.494
2.394
2.344
2.263
2.215
2.163
2.110
1.318
1.295
0.249
1.910
2.027
0.960
1.008
1.004
2.065
6.000
8.928
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0



4c

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$



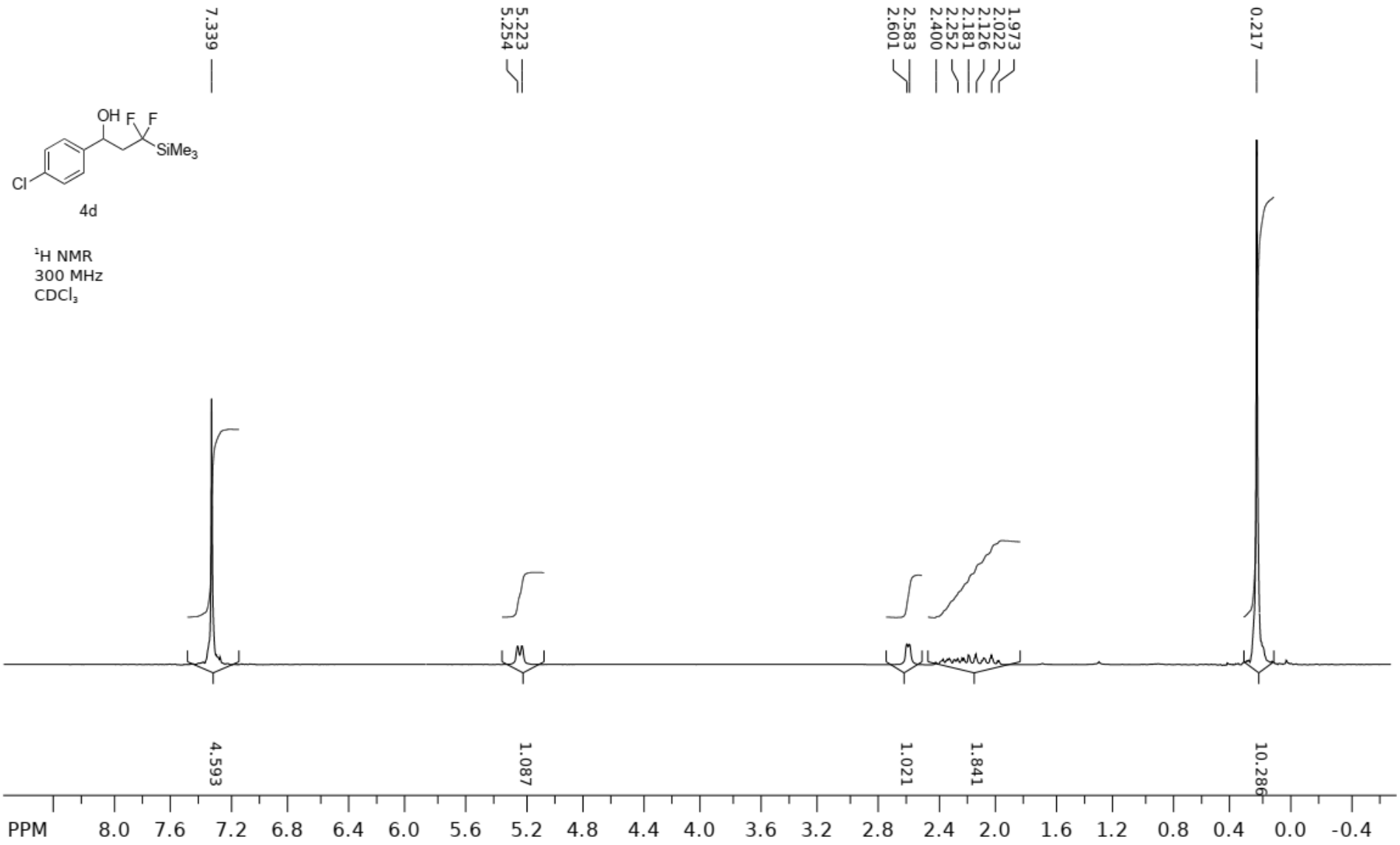
4c

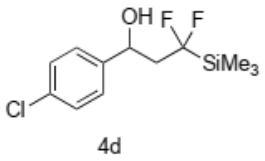
^{19}F NMR
282 MHz
$CDCl_3$

-112.764
-112.812
-112.866
-112.915
-113.881
-113.929
-113.983
-114.032
-114.550
-114.599
-114.662
-114.710
-115.668
-115.717
-115.779
-115.828

1.000
1.001

PPM -84 -88 -92 -96 -100 -104 -108 -112 -116 -120 -124 -128 -132 -136 -140 -144 -148


7.339
5.223
5.254
2.583
2.601
2.400
2.252
2.181
2.126
2.022
1.973
0.217
OH
F
F
SiMe3
Cl
4d
1H NMR
300 MHz
CDCl3
4.593
1.087
1.021
1.841
10.286
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4

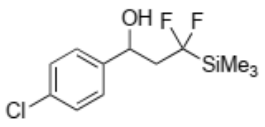


4d

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

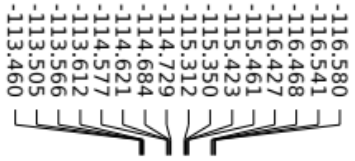
142.545
134.109
133.408
130.687
128.789
127.179
77.584
77.160
76.739
68.137
68.056
68.035
67.952
45.445
45.196
44.954
-4.597

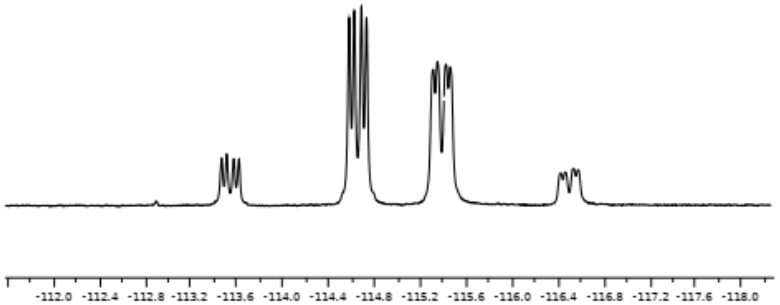
PPM 180 160 140 120 100 80 60 40 20 0

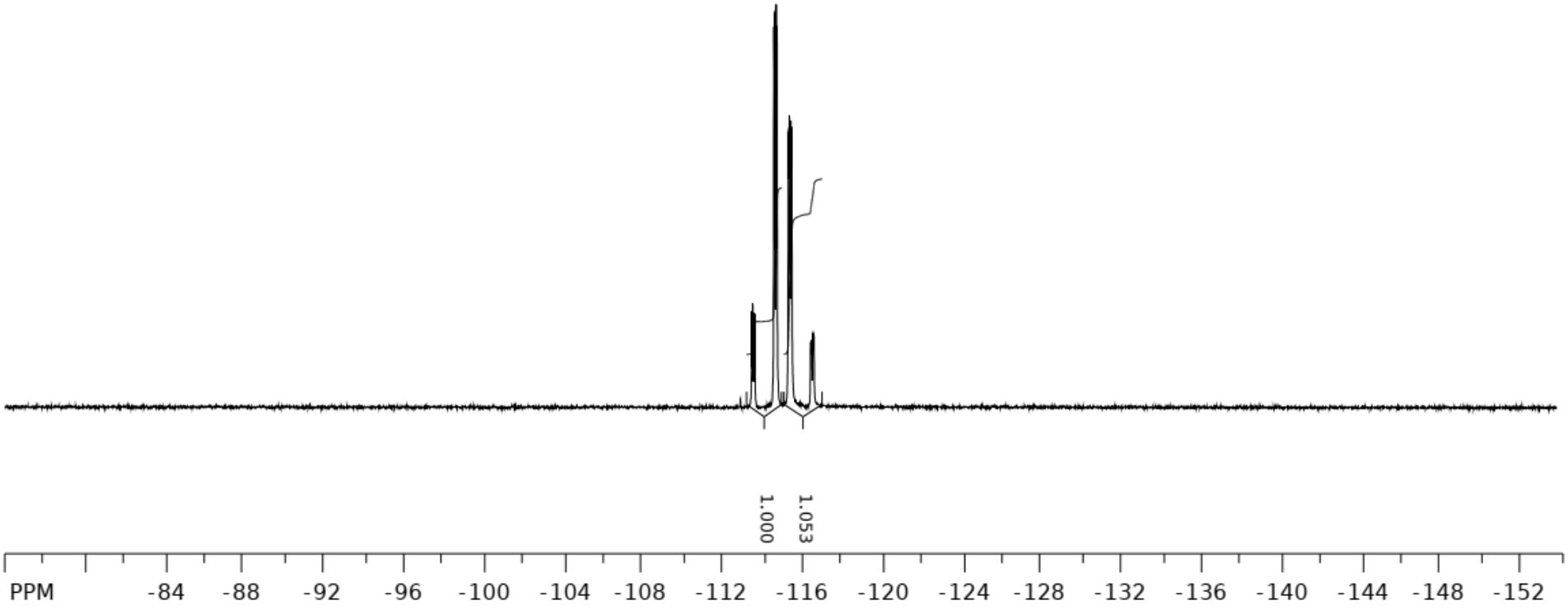


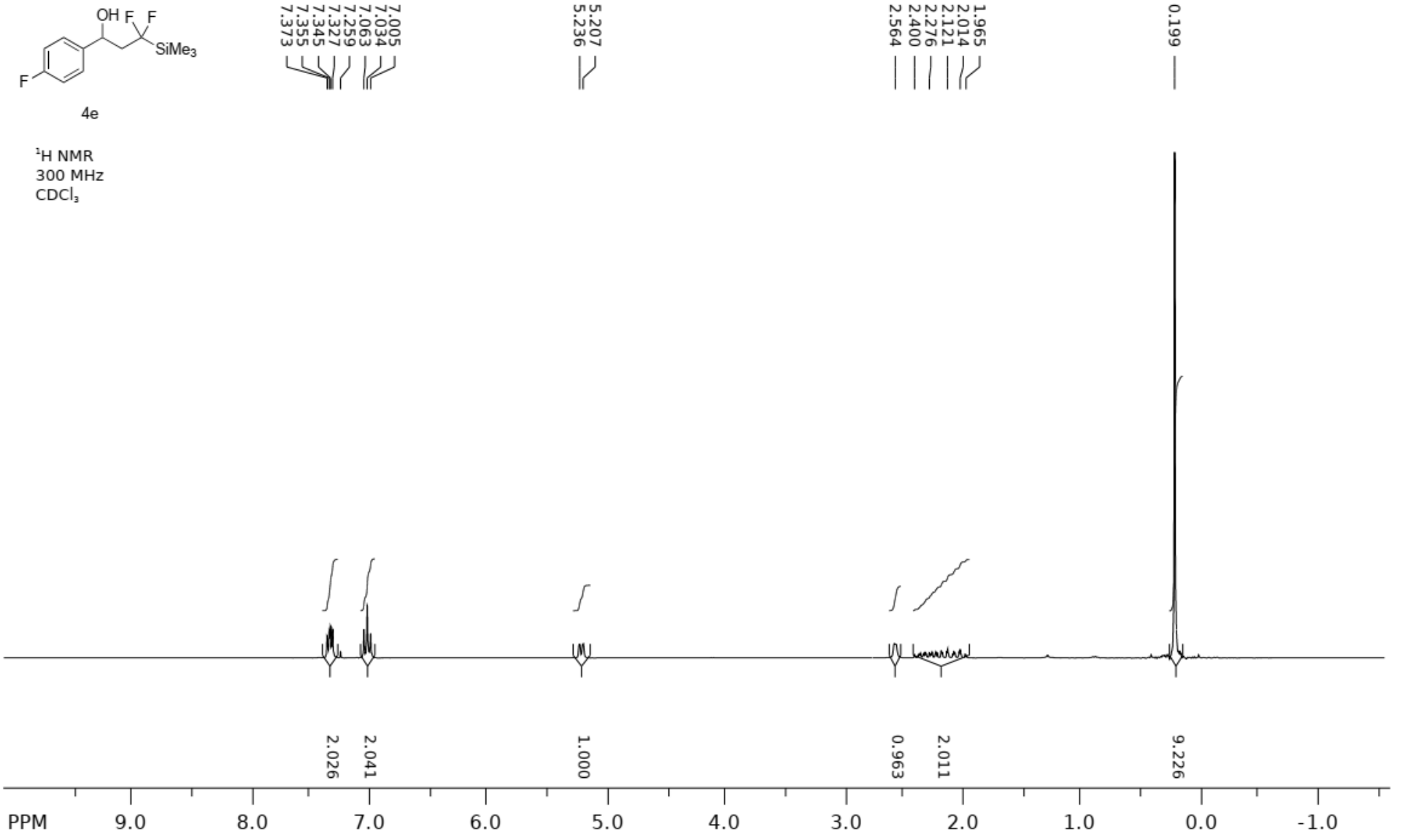
4d

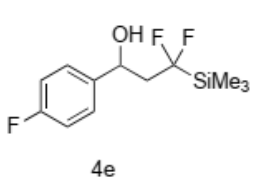
^{19}F NMR
282 MHz
$CDCl_3$





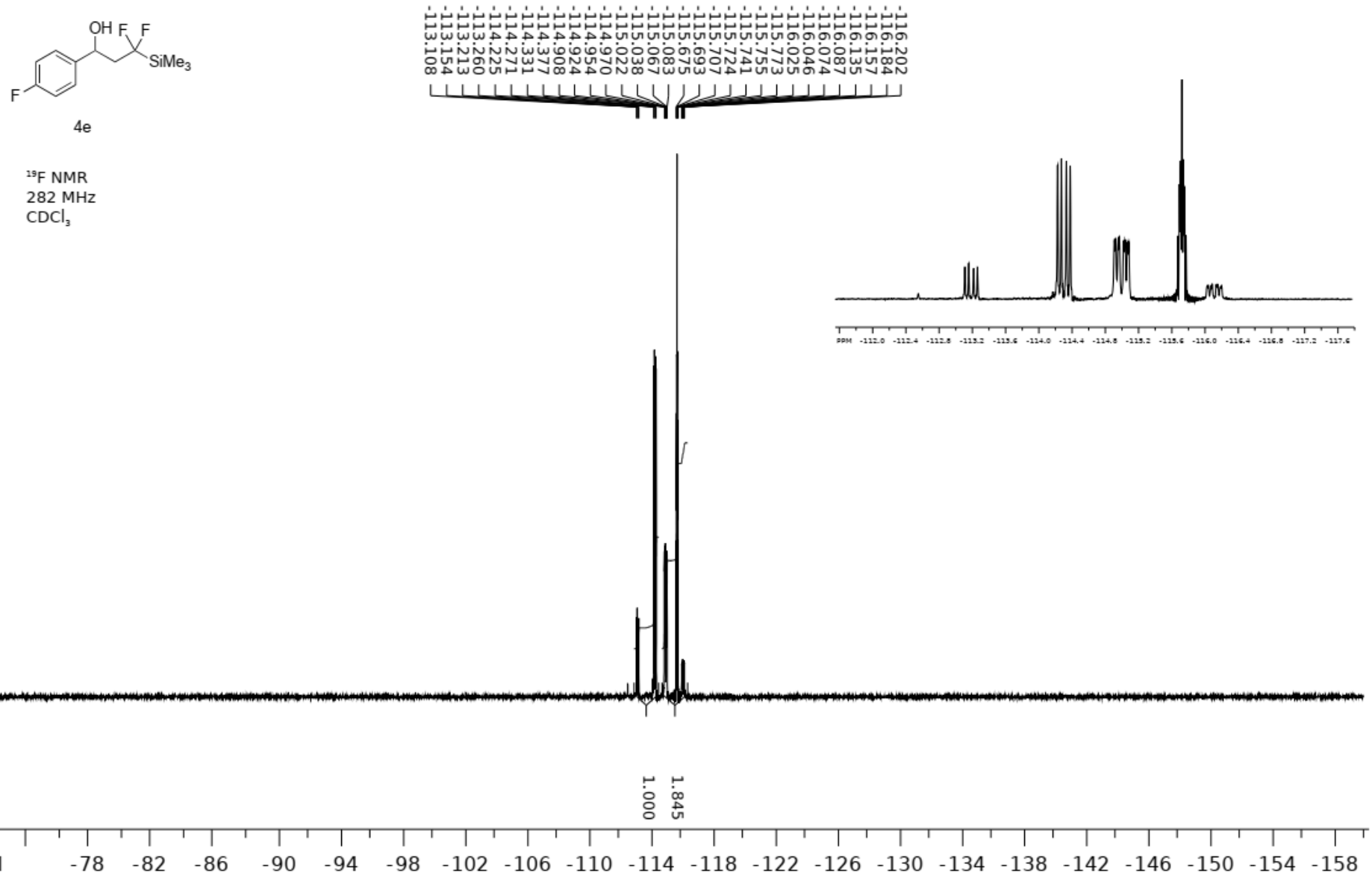


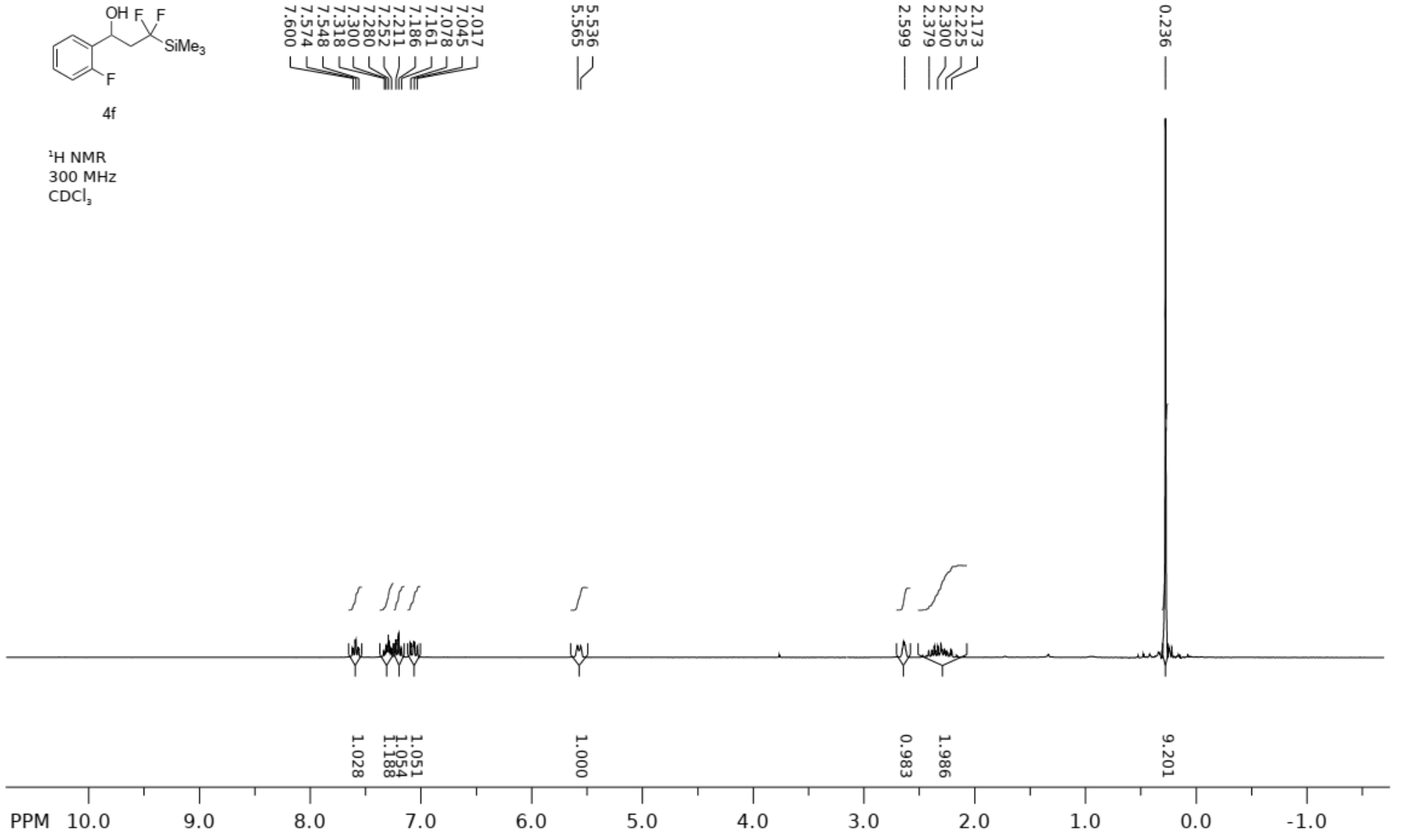

OH F F
SiMe3
F
4e
1H NMR
300 MHz
CDCl3
7.373
7.355
7.345
7.327
7.259
7.063
7.034
7.005
5.236
5.207
2.564
2.400
2.276
2.121
2.014
1.965
0.199
2.026
2.041
1.000
0.963
2.011
9.226
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

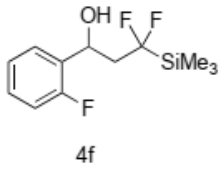


4e

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

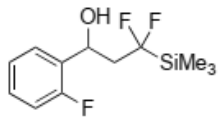

OH F F
SiMe3
F
4e
19F NMR
282 MHz
CDCl3
-113.108
-113.154
-113.213
-113.260
-114.225
-114.271
-114.331
-114.377
-114.908
-114.924
-114.954
-114.970
-115.022
-115.038
-115.067
-115.083
-115.675
-115.693
-115.707
-115.724
-115.741
-115.755
-115.773
-116.025
-116.046
-116.074
-116.087
-116.135
-116.157
-116.184
-116.202
1.000
1.845
PPM
-78 -82 -86 -90 -94 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150 -154 -158


OH F F
SiMe3
F
4f
1H NMR
300 MHz
CDCl3
7.600
7.574
7.548
7.318
7.300
7.280
7.252
7.211
7.186
7.161
7.078
7.045
7.017
5.565
5.536
2.599
2.379
2.300
2.225
2.173
0.236
1.028
1.188
1.054
1.051
1.000
0.983
1.986
9.201
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0



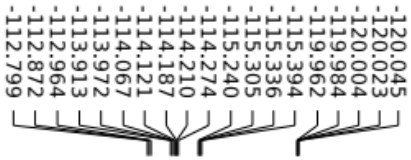
4f

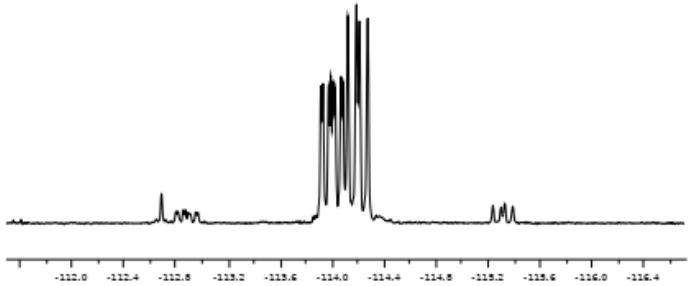
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

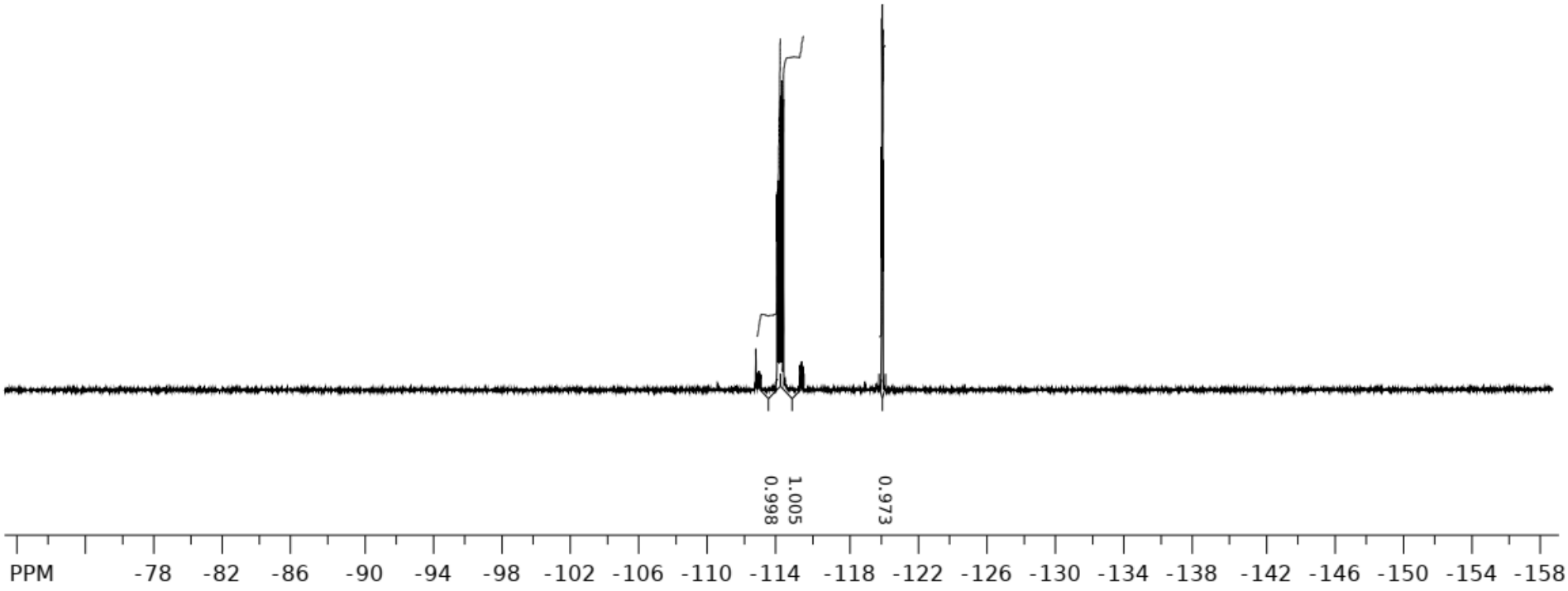


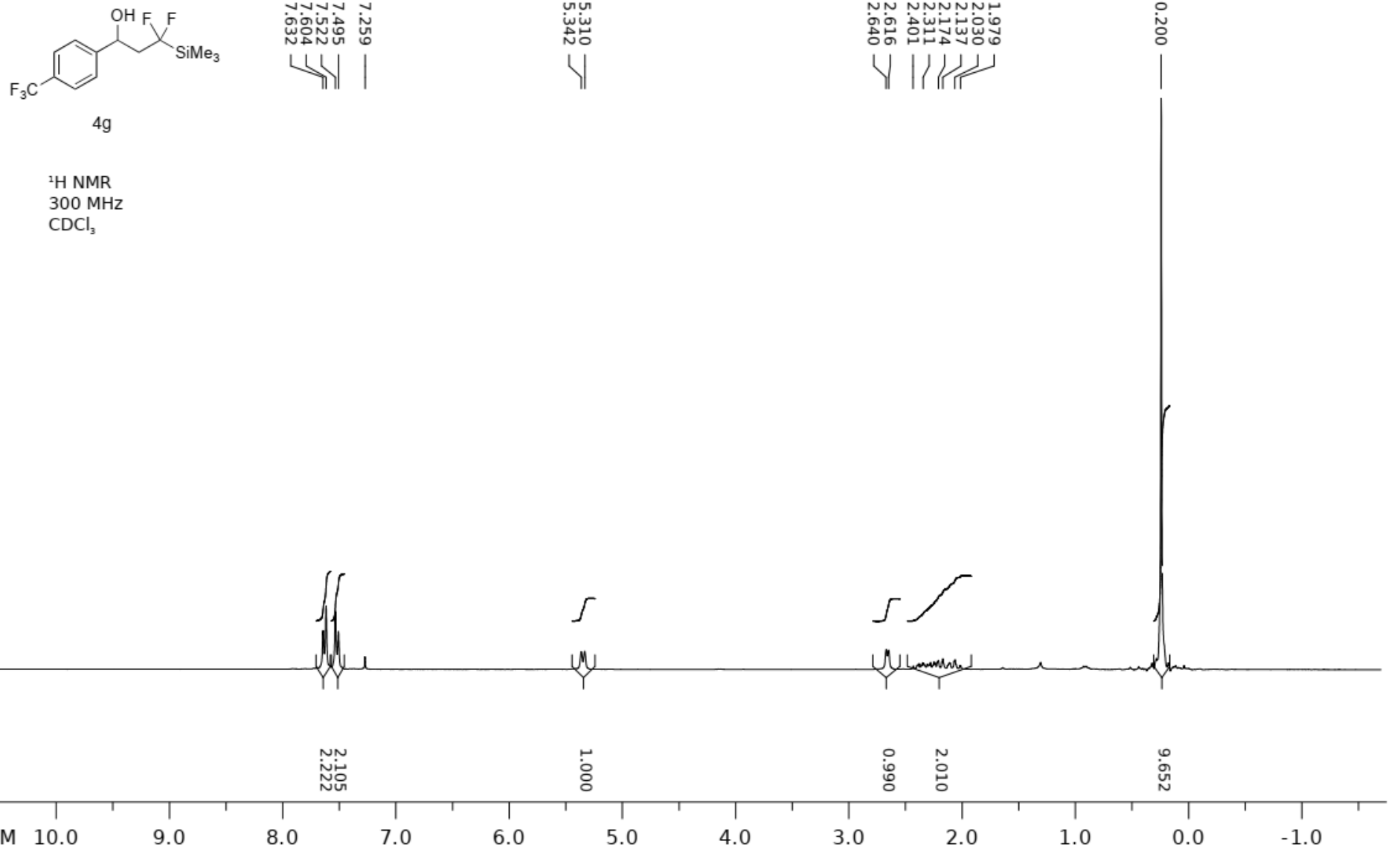
4f

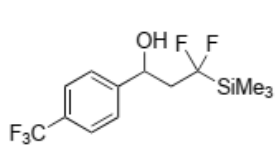
^{19}F NMR
282 MHz
$CDCl_3$







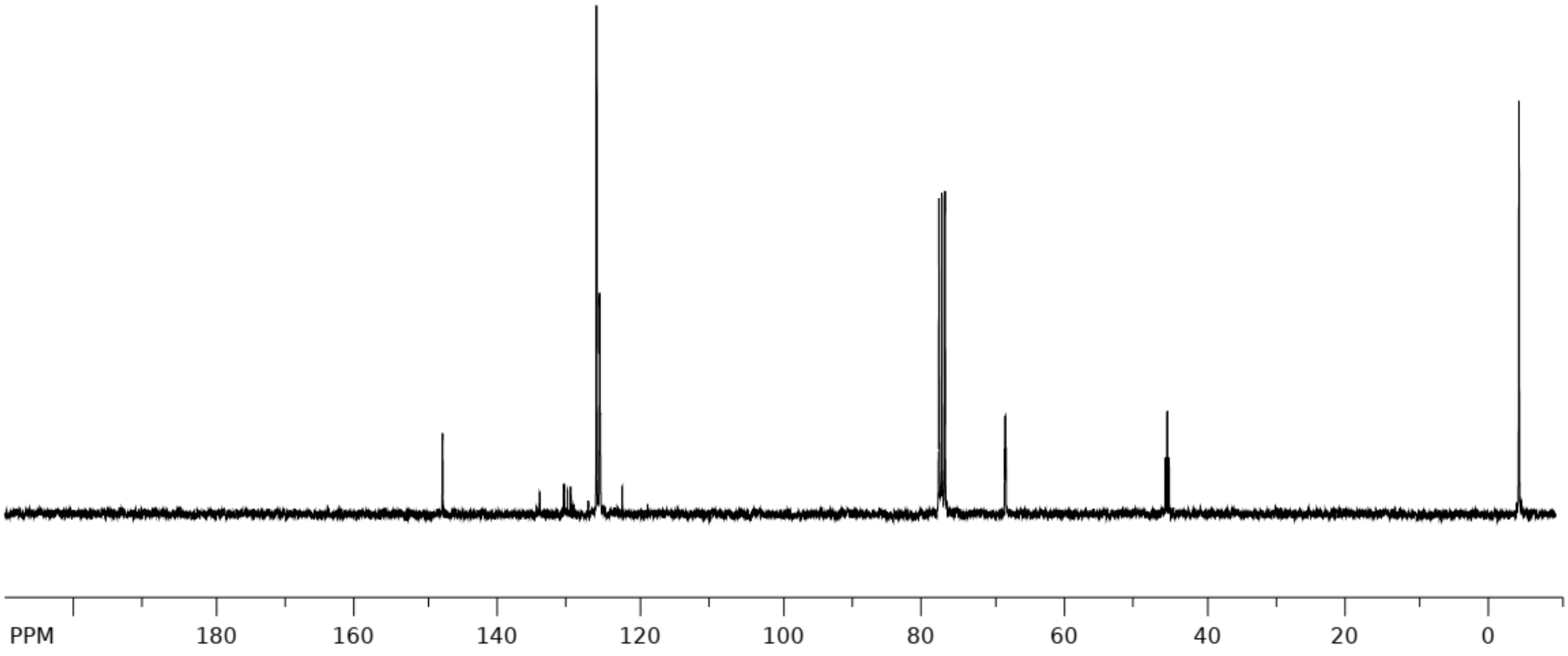

OH
F
F
SiMe3
F3C
4g
1H NMR
300 MHz
CDCl3
7.632
7.604
7.522
7.495
7.259
5.342
5.310
2.640
2.616
2.401
2.311
2.174
2.137
2.030
1.979
0.200
2.222
2.105
1.000
0.990
2.010
9.652
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

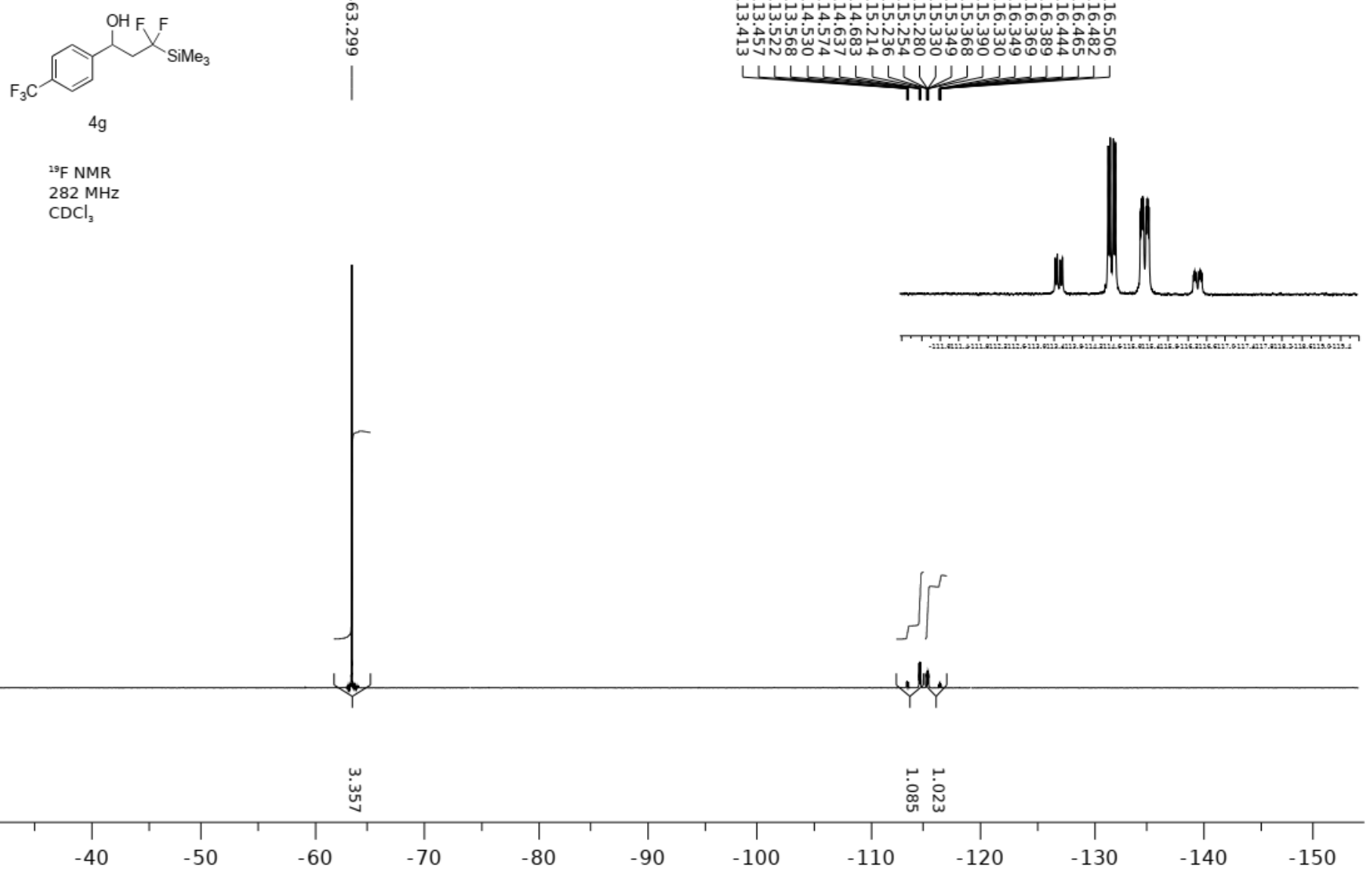


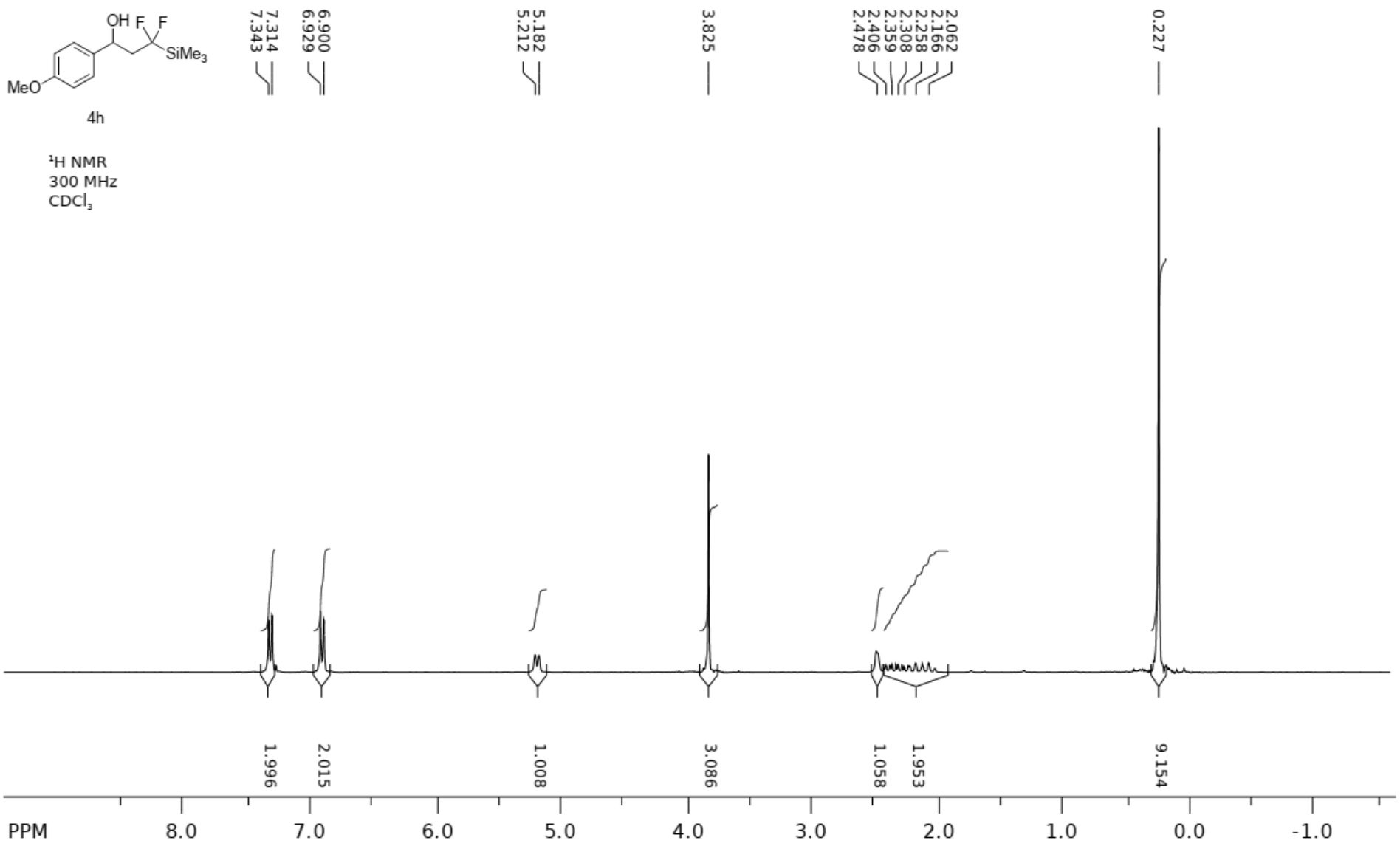
4g

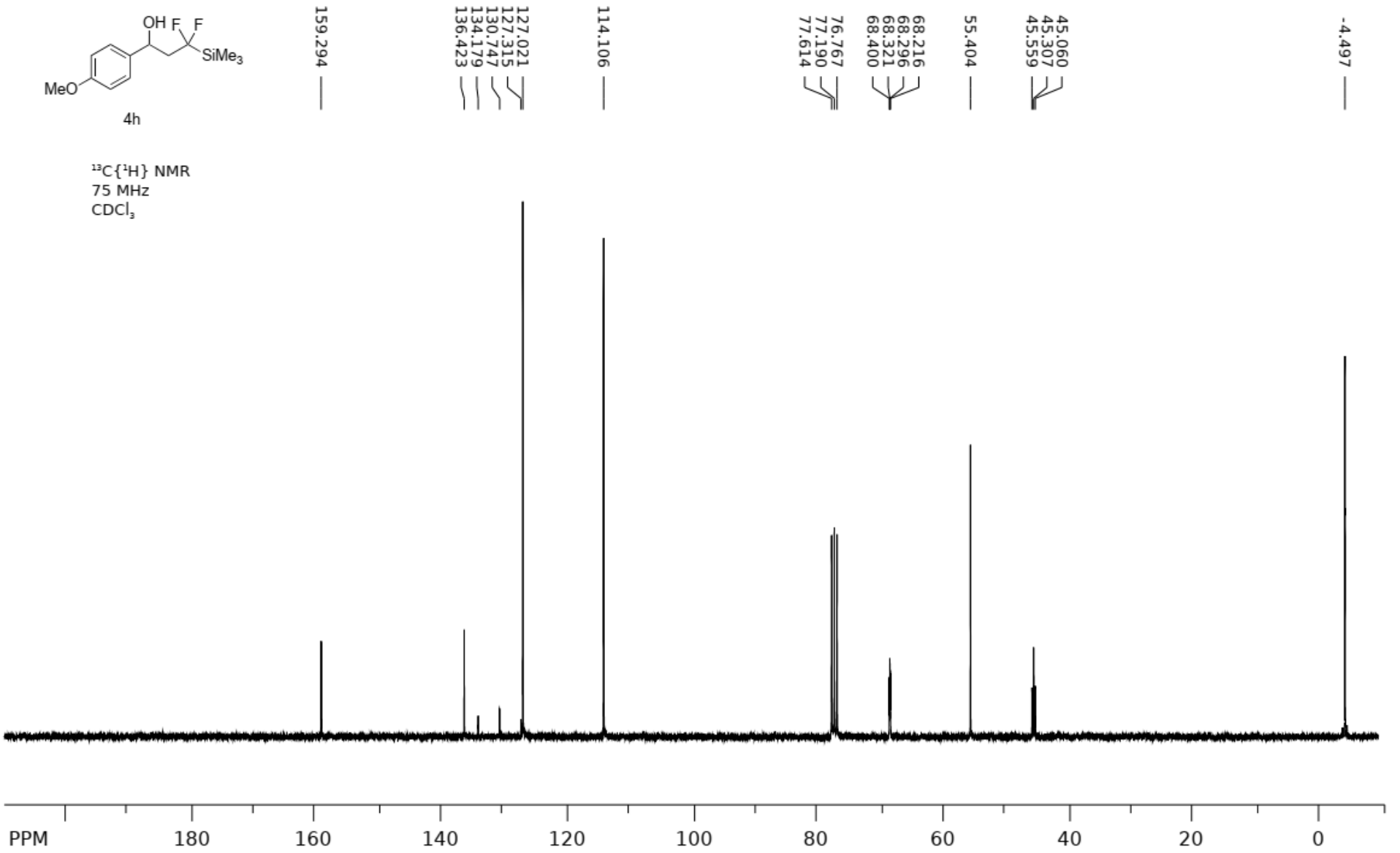
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

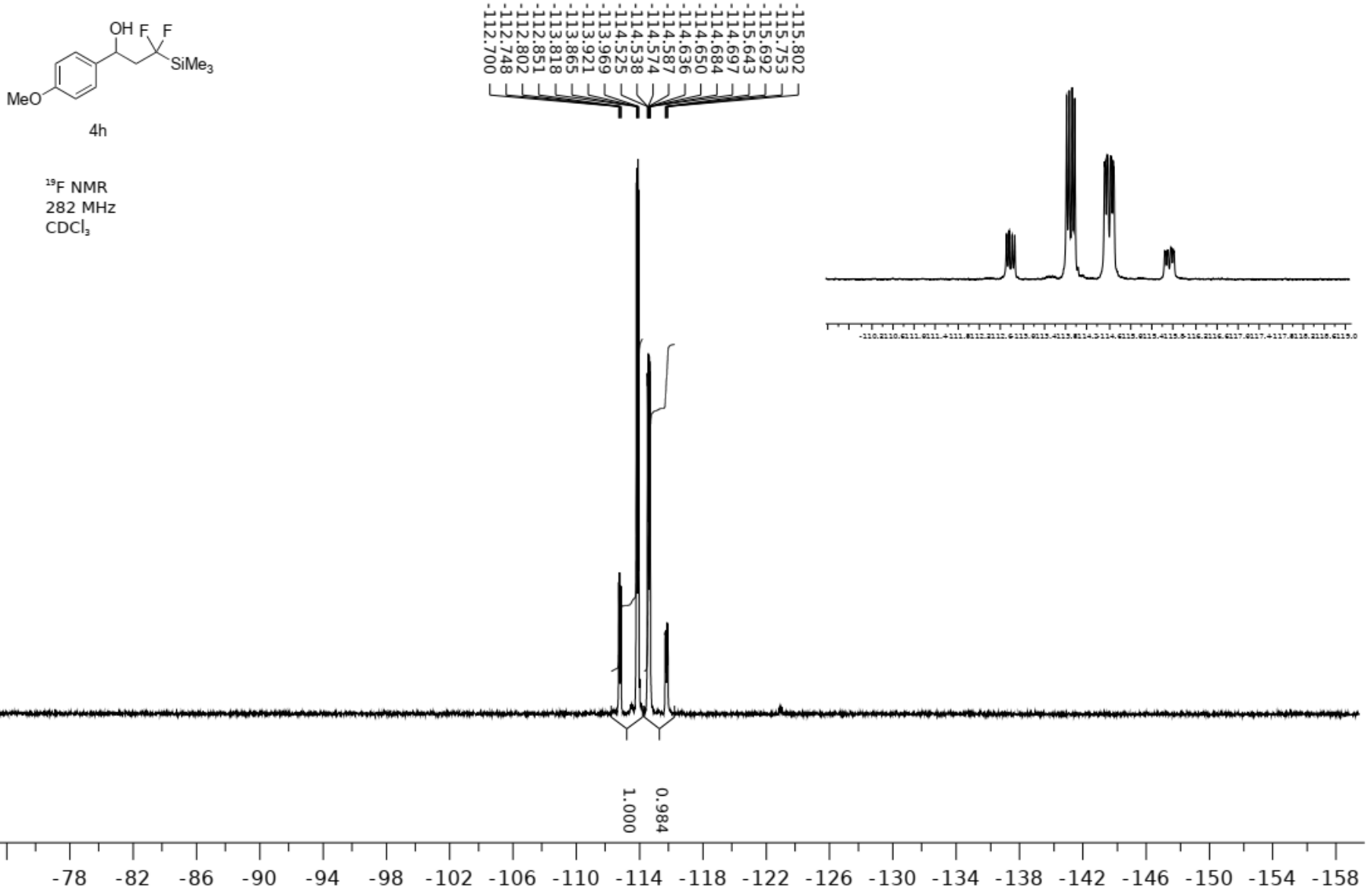
147.950
134.150
130.734
130.654
130.235
129.804
129.692
129.369
127.278
126.157
125.726
125.676
125.628
125.581
122.487
118.880
77.583
77.160
76.737
68.267
68.176
68.082
45.452
45.212
44.962
-4.629

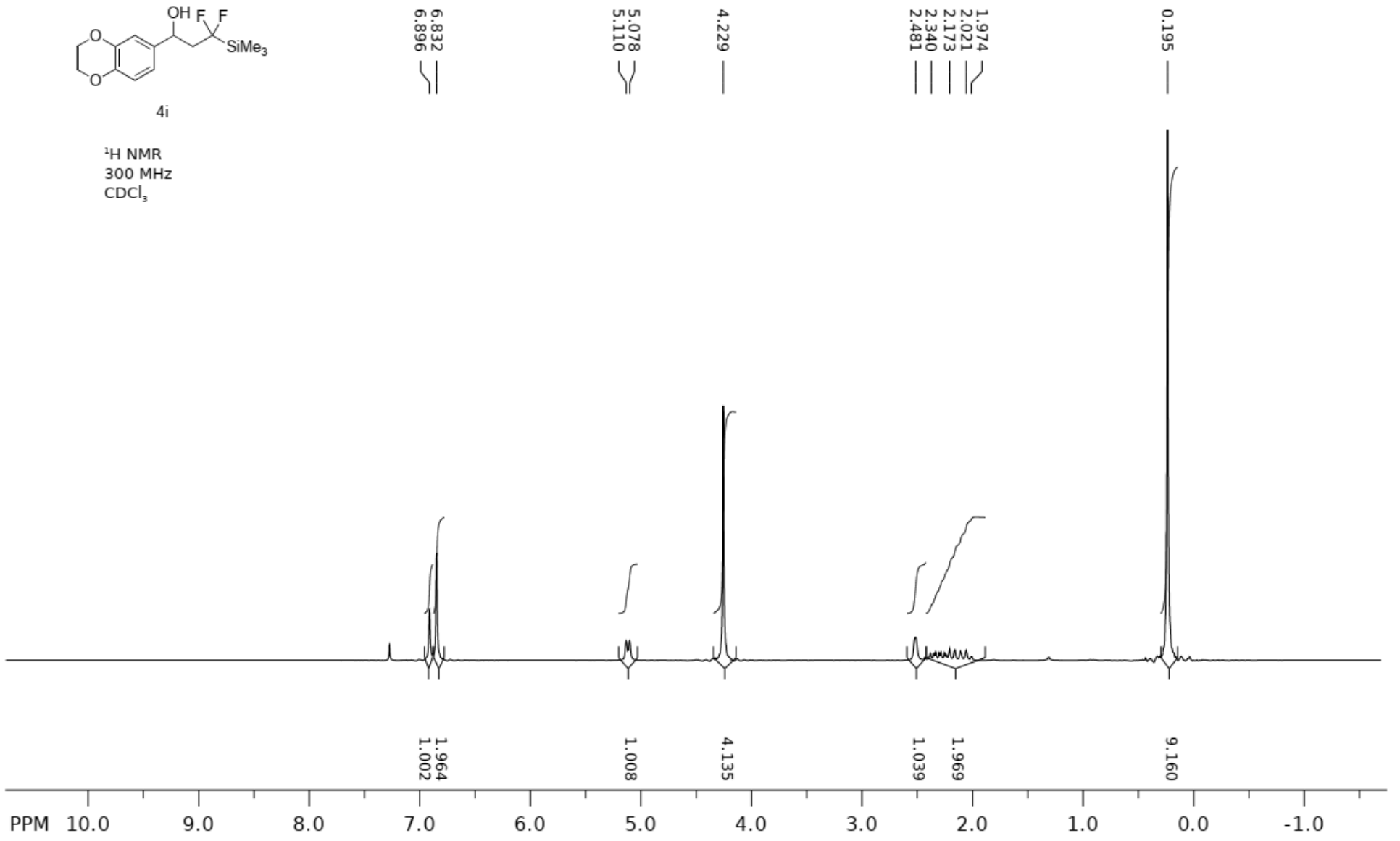


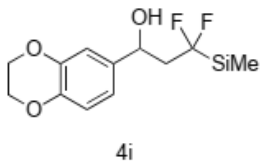

OH F F
SiMe3
F3C
4g
19F NMR
282 MHz
CDCl3
-63.299
-113.413
-113.457
-113.522
-113.568
-114.530
-114.574
-114.637
-114.683
-115.214
-115.236
-115.254
-115.280
-115.330
-115.349
-115.368
-115.390
-116.330
-116.349
-116.369
-116.389
-116.444
-116.465
-116.482
-116.506
3.357
1.085
1.023
PPM
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150


OH F F
SiMe3
MeO
4h
1H NMR
300 MHz
CDCl3
7.314
7.343
6.900
6.929
5.182
5.212
3.825
2.478
2.406
2.359
2.308
2.258
2.166
2.062
0.227
1.996
2.015
1.008
3.086
1.058
1.953
9.154
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


OH F F
SiMe3
MeO
4h
159.294
136.423
134.179
130.747
127.315
127.021
114.106
77.614
77.190
76.767
68.400
68.321
68.296
68.216
55.404
45.559
45.307
45.060
-4.497
13C{1H} NMR
75 MHz
CDCl3
PPM
180
160
140
120
100
80
60
40
20
0


OH F F
SiMe3
MeO
4h
19F NMR
282 MHz
CDCl3
-112.700
-112.748
-112.802
-112.851
-113.818
-113.865
-113.921
-113.969
-114.525
-114.538
-114.574
-114.587
-114.636
-114.650
-114.684
-114.697
-115.643
-115.692
-115.753
-115.802
1.000
0.984
PPM
-78 -82 -86 -90 -94 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150 -154 -158


OH F F
SiMe3
O
O
4i
1H NMR
300 MHz
CDCl3
6.832
6.896
5.078
5.110
4.229
2.481
2.340
2.173
2.021
1.974
0.195
1.964
1.002
1.008
4.135
1.039
1.969
9.160
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

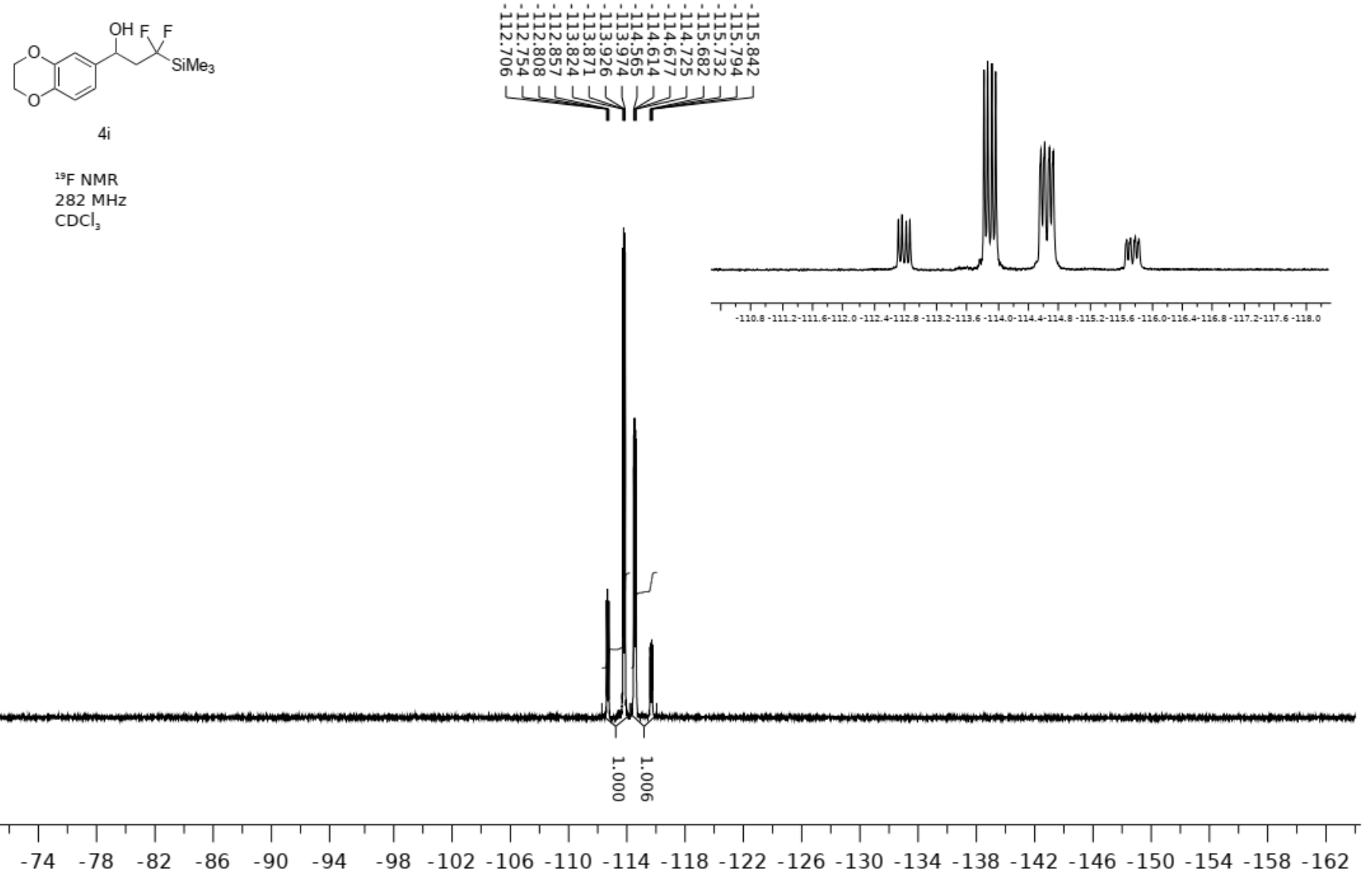


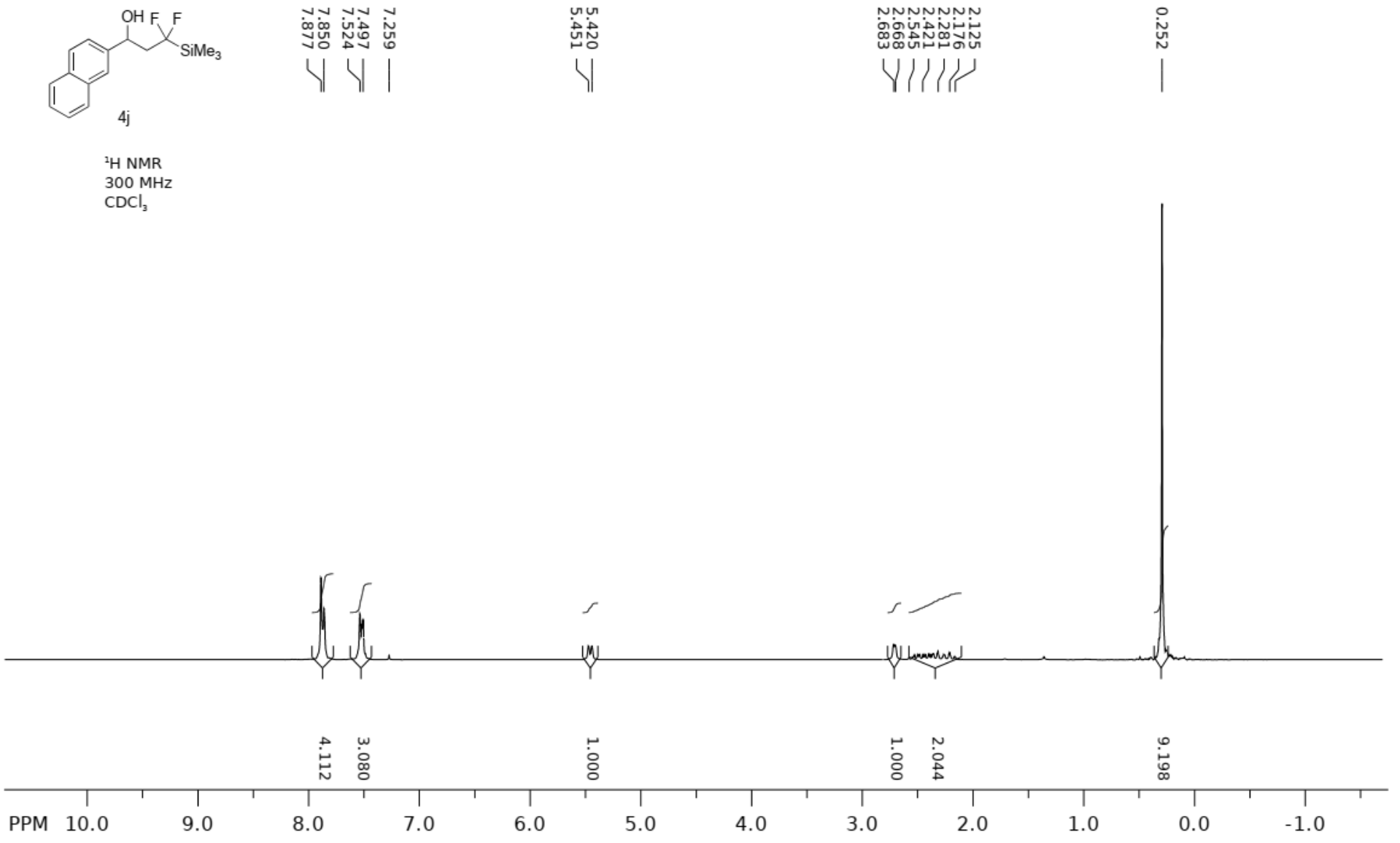
4i

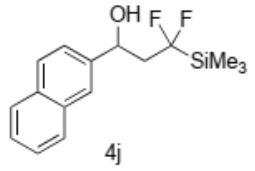
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

143.083
143.583
137.571
134.073
130.643
127.213
114.733
117.334
118.744
76.736
77.160
77.584
64.429
68.061
68.146
68.239
44.934
45.190
45.437
-4.545

PPM 180 160 140 120 100 80 60 40 20 0

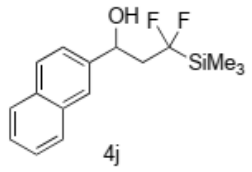

OH F F
SiMe3
O
O
4i
19F NMR
282 MHz
CDCl3
-112.706
-112.754
-112.808
-112.857
-113.824
-113.871
-113.926
-113.974
-114.565
-114.614
-114.677
-114.725
-115.682
-115.732
-115.794
-115.842
-110.8 -111.2 -111.6 -112.0 -112.4 -112.8 -113.2 -113.6 -114.0 -114.4 -114.8 -115.2 -115.6 -116.0 -116.4 -116.8 -117.2 -117.6 -118.0
1.000
1.006
PPM
-74 -78 -82 -86 -90 -94 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150 -154 -158 -162


OH F F
SiMe3
4j
1H NMR
300 MHz
CDCl3
7.877
7.850
7.524
7.497
7.259
5.451
5.420
2.683
2.668
2.545
2.421
2.281
2.176
2.125
0.252
4.112
3.080
1.000
1.000
2.044
9.198
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0



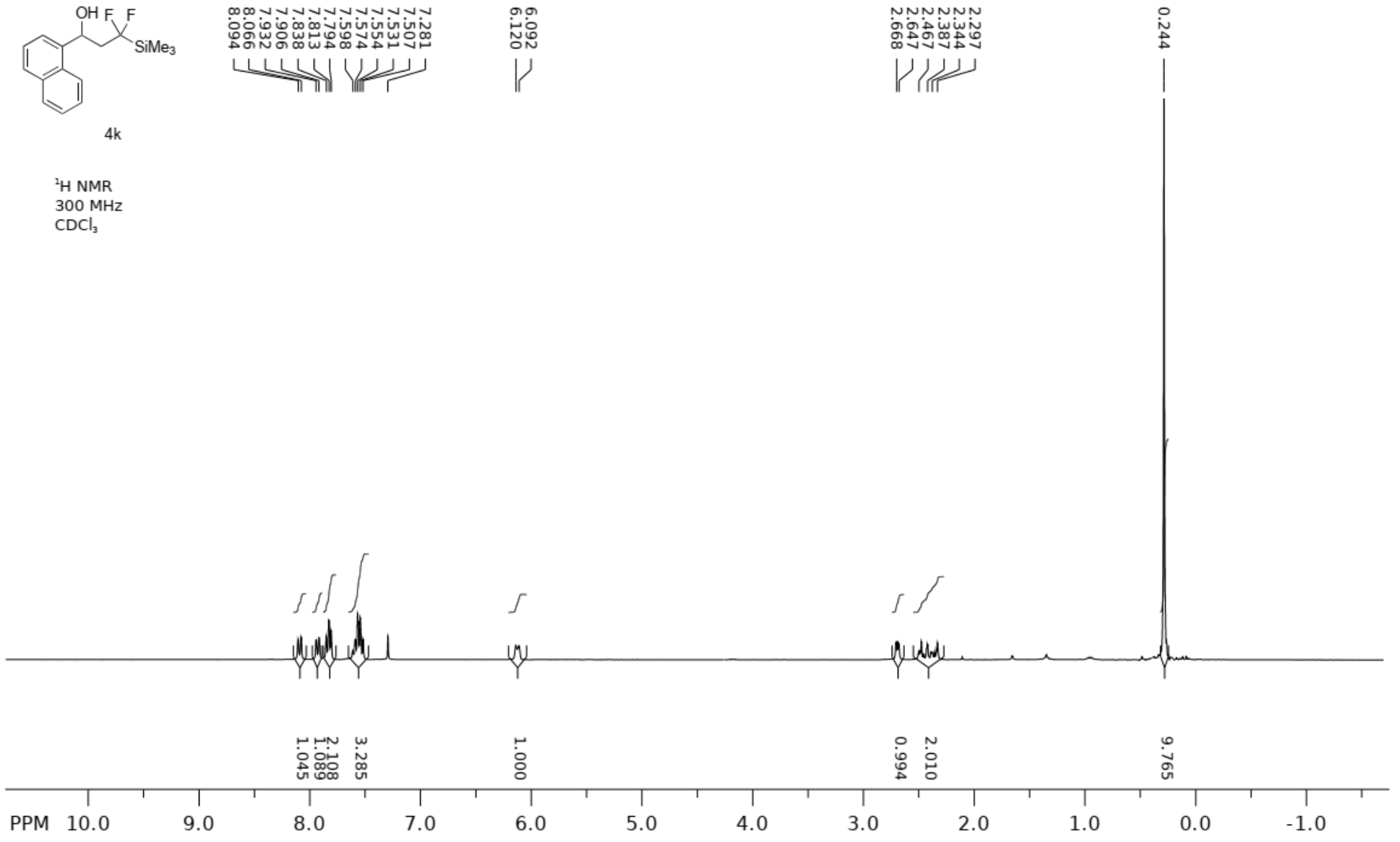
4j

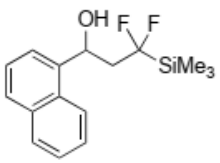
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$



4j

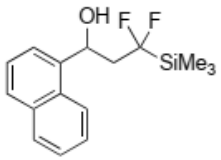
^{19}F NMR
282 MHz
$CDCl_3$


OH F F
SiMe3
4k
1H NMR
300 MHz
CDCl3
8.094
8.066
7.932
7.906
7.838
7.813
7.794
7.598
7.574
7.554
7.531
7.507
7.281
6.120
6.092
2.668
2.647
2.467
2.387
2.344
2.297
0.244
1.045
2.108
1.089
3.285
1.000
0.994
2.010
9.765
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0



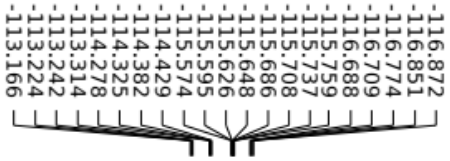
4k

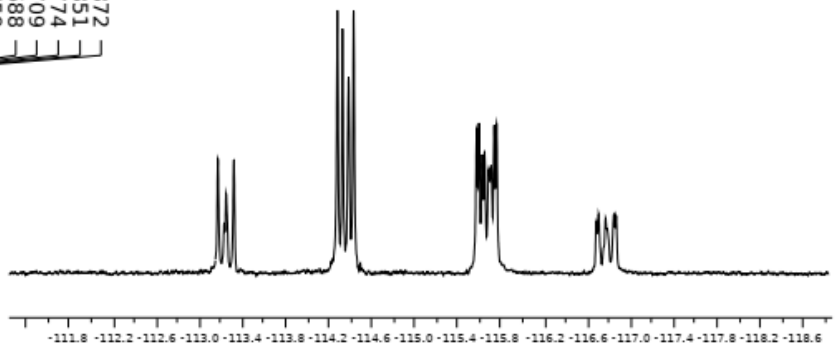
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

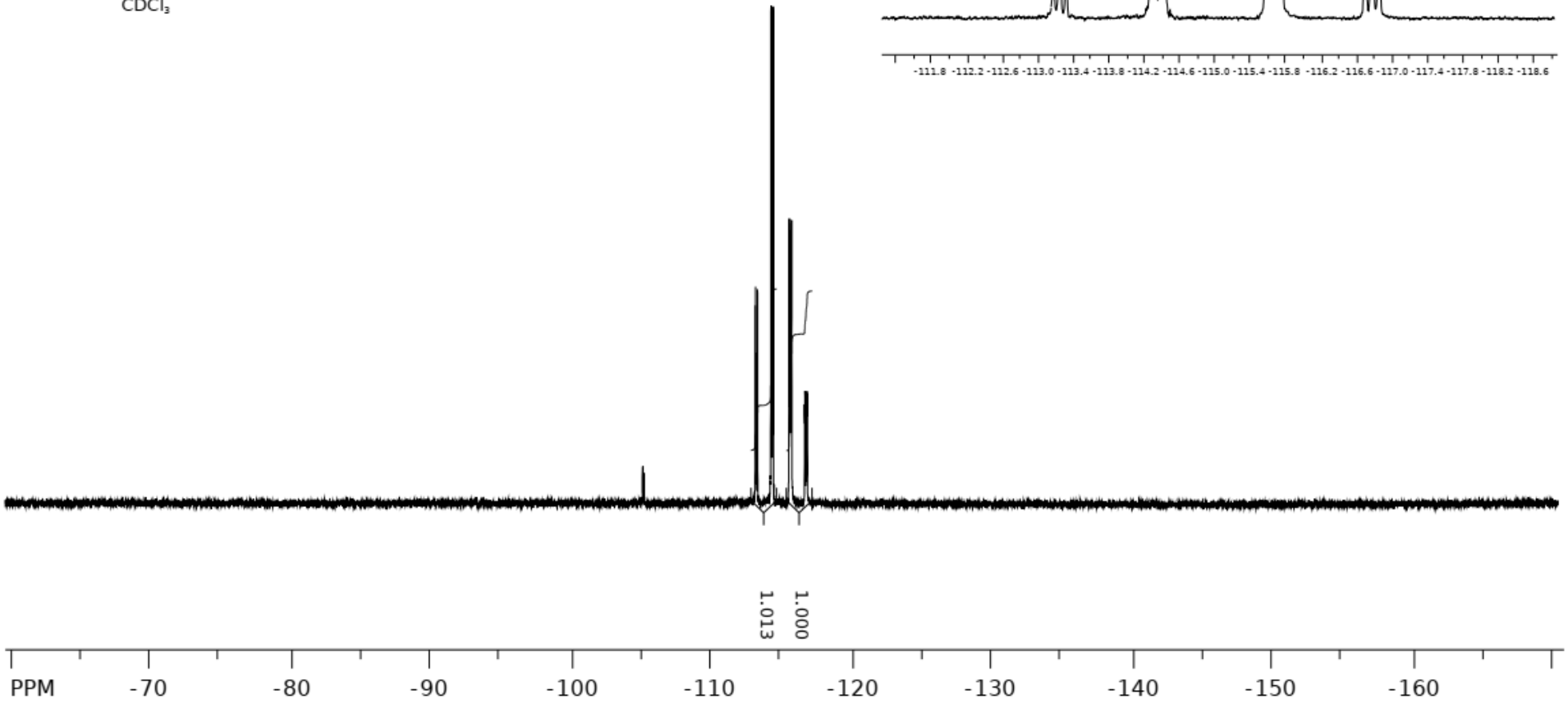


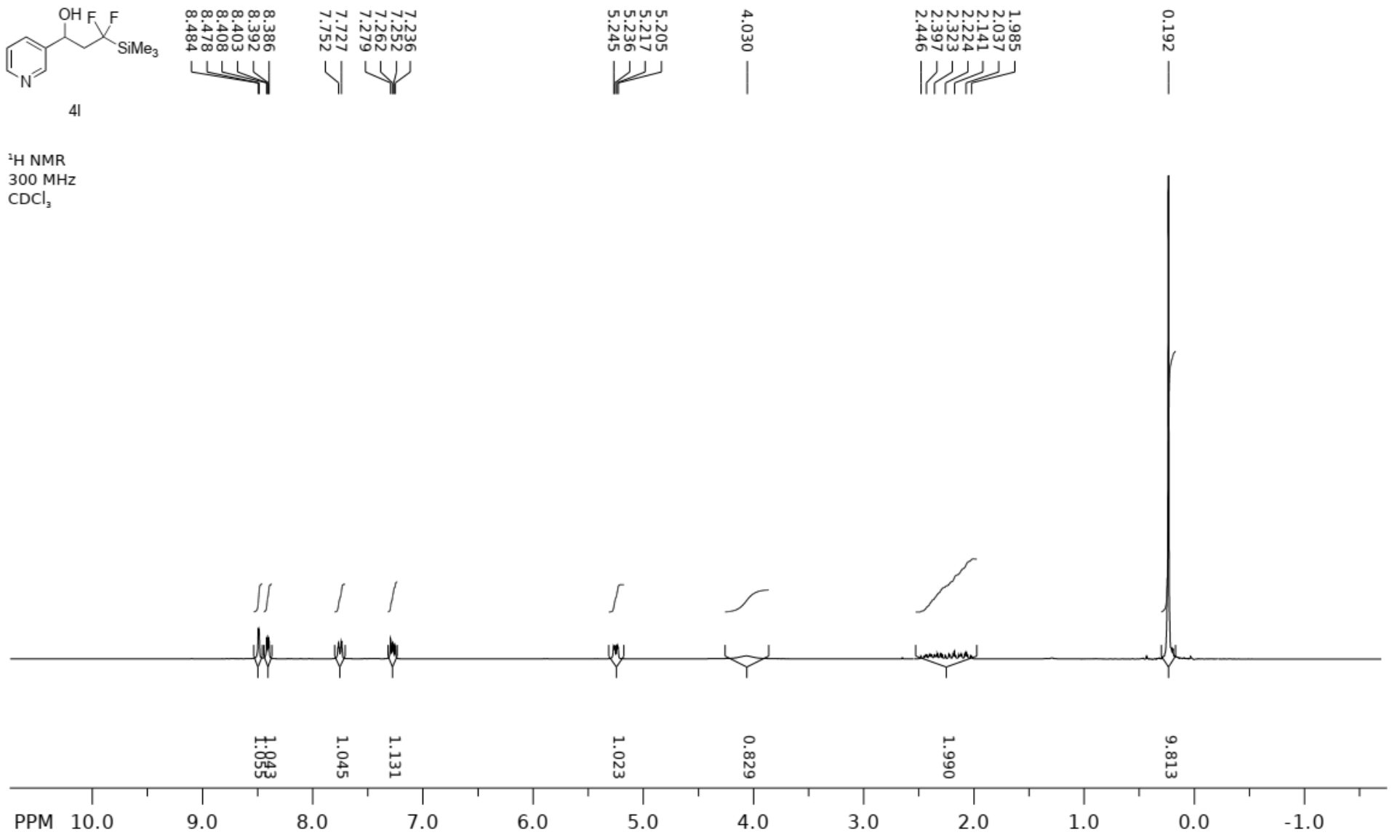
4k

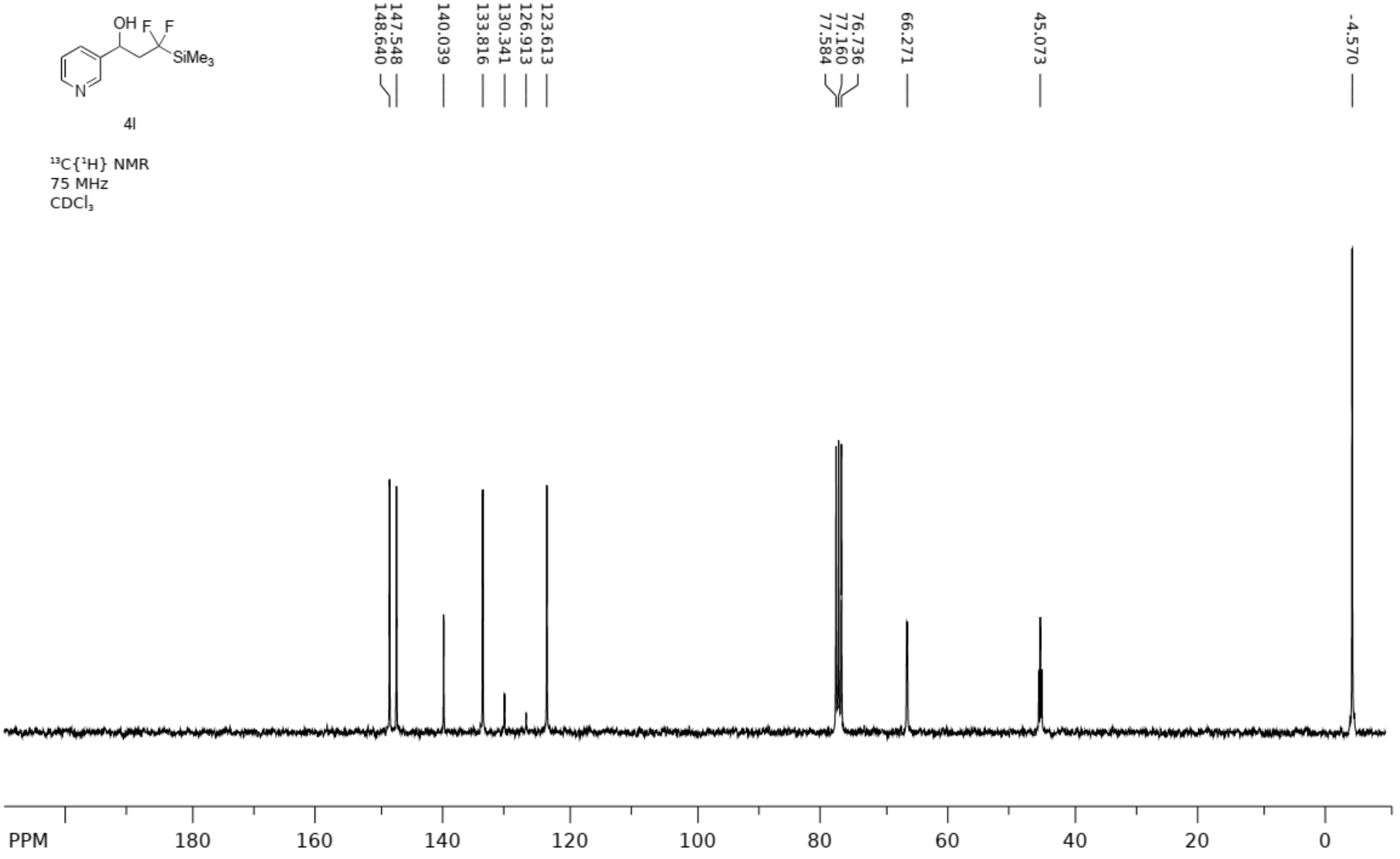
^{19}F NMR
282 MHz
$CDCl_3$

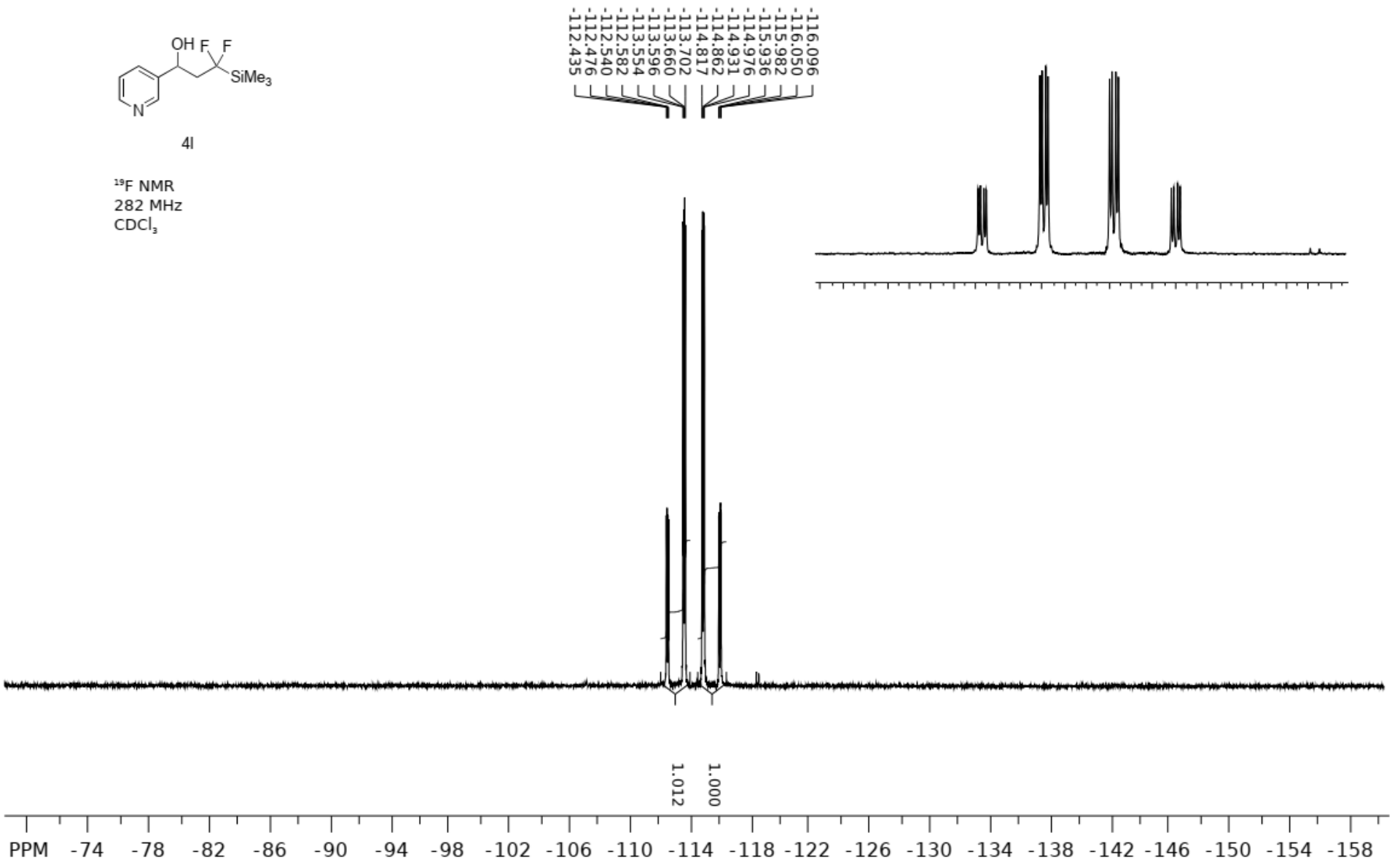


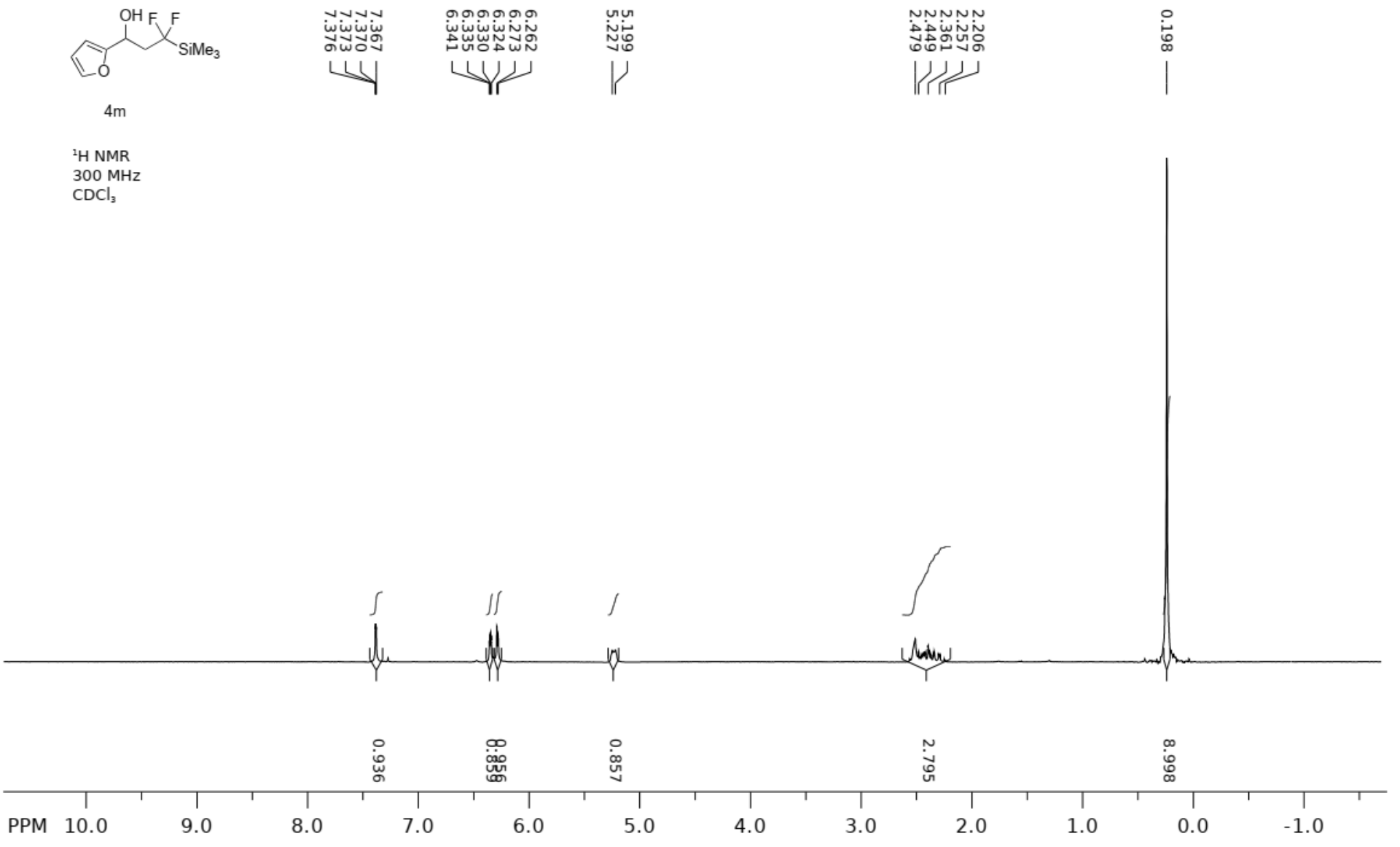


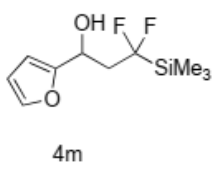



OH
F
F
SiMe3
N
4l
8.386
8.392
8.403
8.408
8.478
8.484
7.727
7.752
7.236
7.252
7.262
7.279
5.205
5.217
5.236
5.245
4.030
1.985
2.037
2.141
2.224
2.323
2.397
2.446
0.192
1H NMR
300 MHz
CDCl3
1.043
1.055
1.045
1.131
1.023
0.829
1.990
9.813
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


OH
F
F
SiMe3
N
4l
13C{1H} NMR
75 MHz
CDCl3
147.548
148.640
140.039
133.816
130.341
126.913
123.613
76.736
77.160
77.584
66.271
45.073
-4.570
PPM
180
160
140
120
100
80
60
40
20
0


OH F F
SiMe3
N
4l
19F NMR
282 MHz
CDCl3
-112.435
-112.476
-112.540
-112.582
-113.554
-113.596
-113.660
-113.702
-114.817
-114.862
-114.931
-114.976
-115.936
-115.982
-116.050
-116.096
1.012
1.000
PPM -74 -78 -82 -86 -90 -94 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150 -154 -158

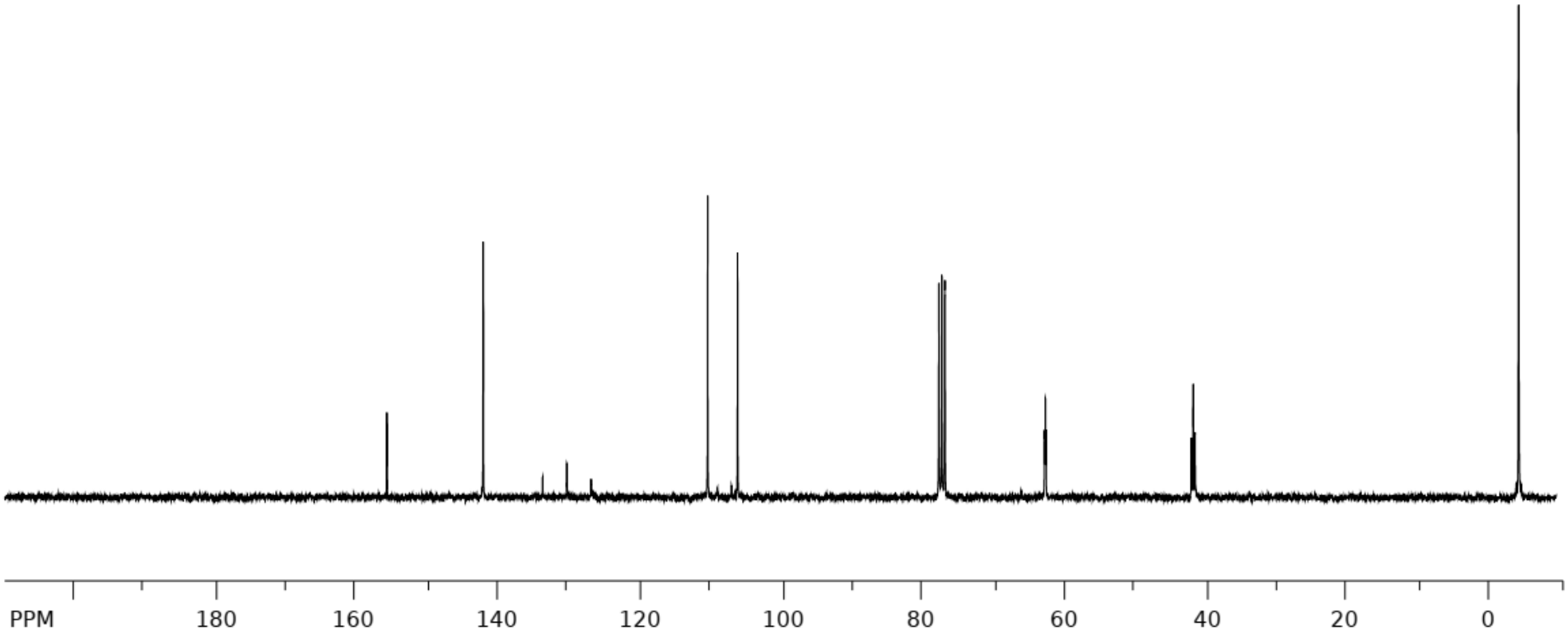

OH
F
F
SiMe3
O
4m
1H NMR
300 MHz
CDCl3
7.376
7.373
7.370
7.367
6.341
6.335
6.330
6.324
6.273
6.262
5.227
5.199
2.479
2.449
2.361
2.257
2.206
0.198
0.936
0.856
0.857
2.795
8.998
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

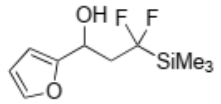


4m

155.825
142.173
133.739
130.305
126.871
110.360
106.114
77.584
77.160
76.736
62.604
62.517
62.492
62.403
41.791
41.535
41.284
-4.553
-4.582

$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

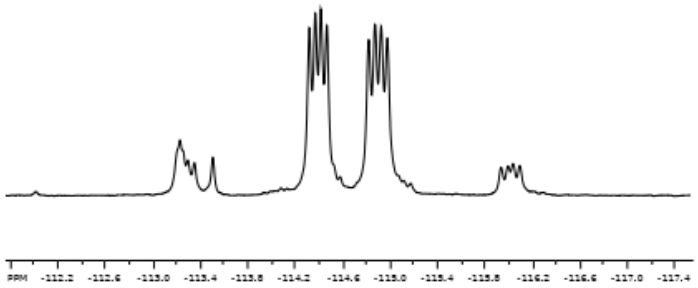


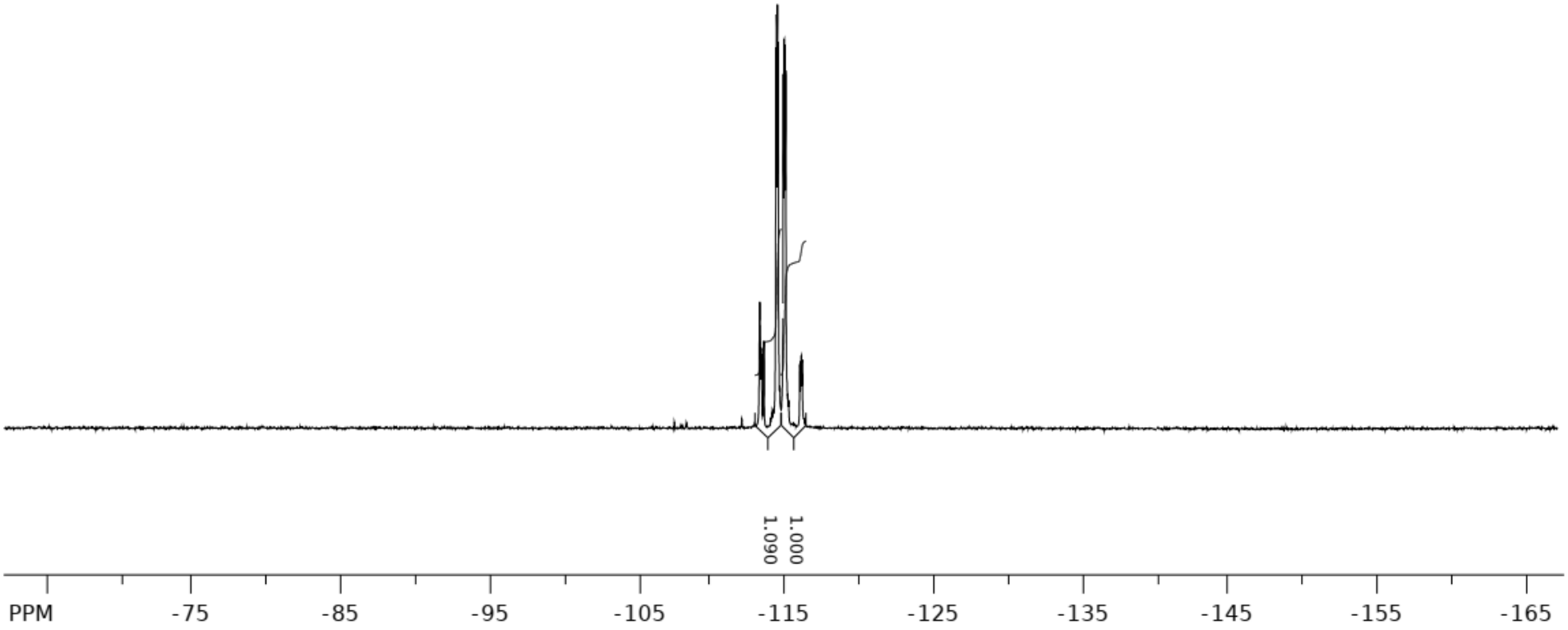


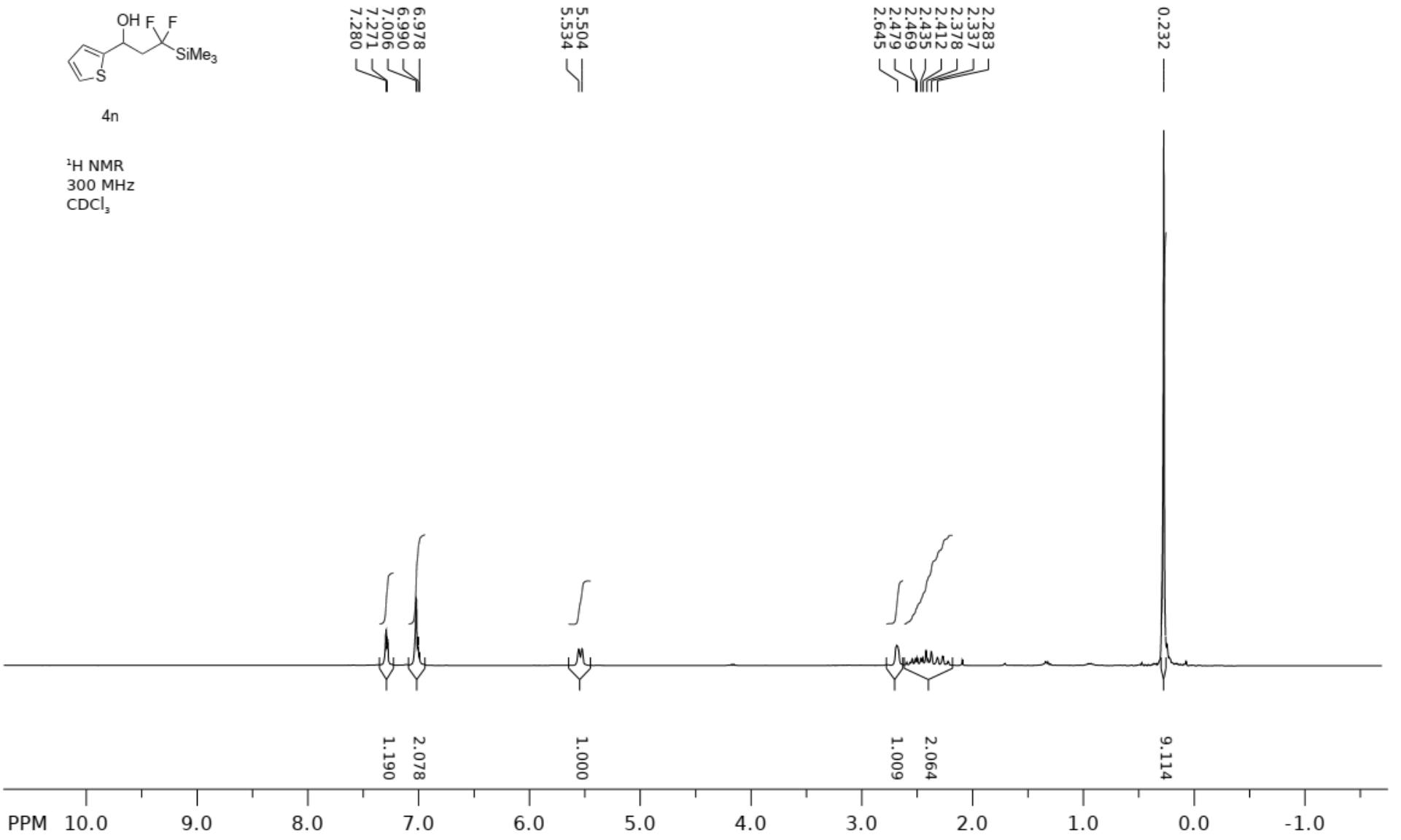
4m

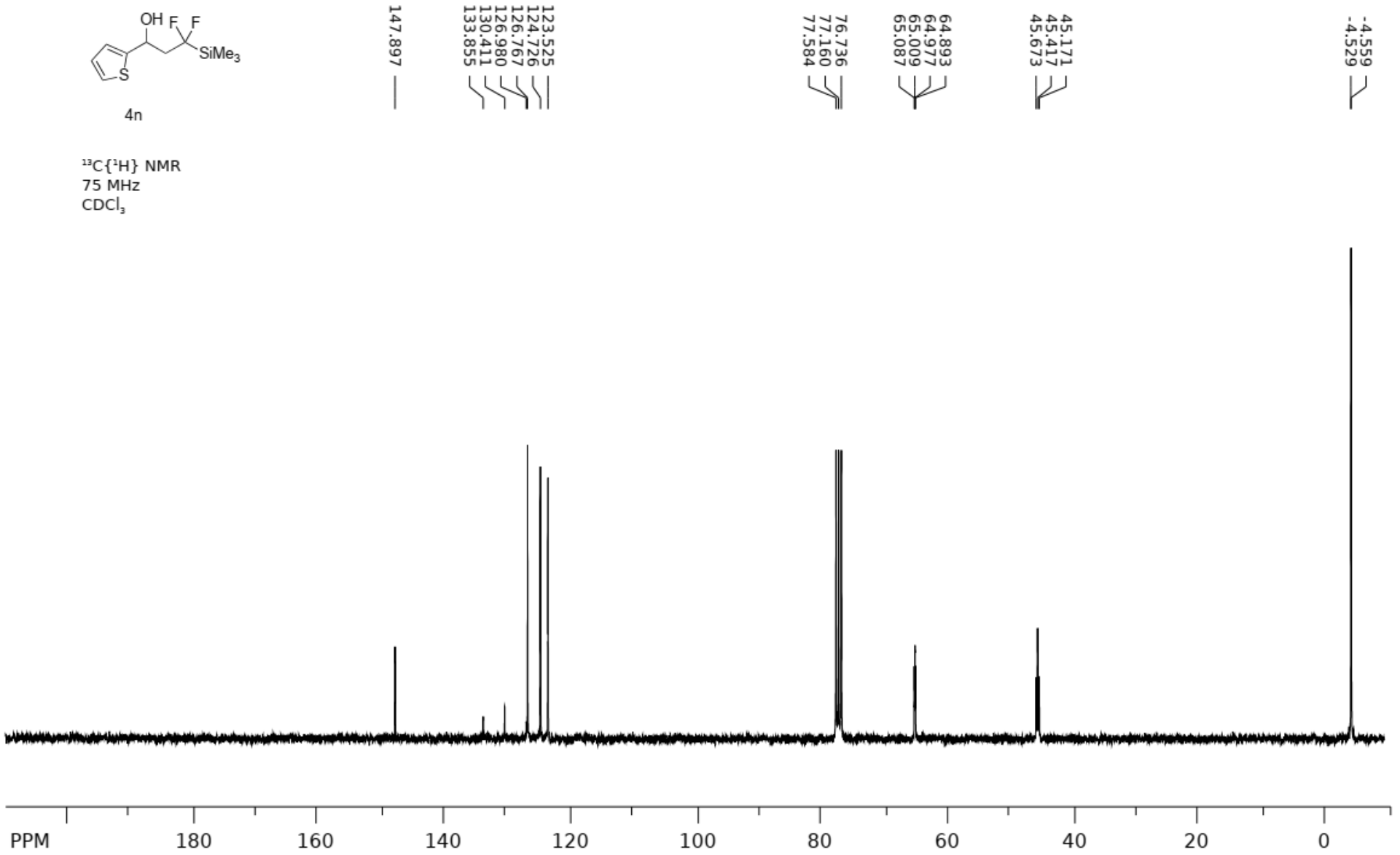
^{19}F NMR
282 MHz
$CDCl_3$

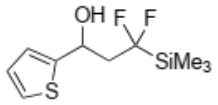
-113.290
-113.345
-113.501
-114.318
-114.368
-114.415
-114.465
-114.819
-114.873
-114.924
-114.976
-115.939
-115.997
-116.040
-116.097





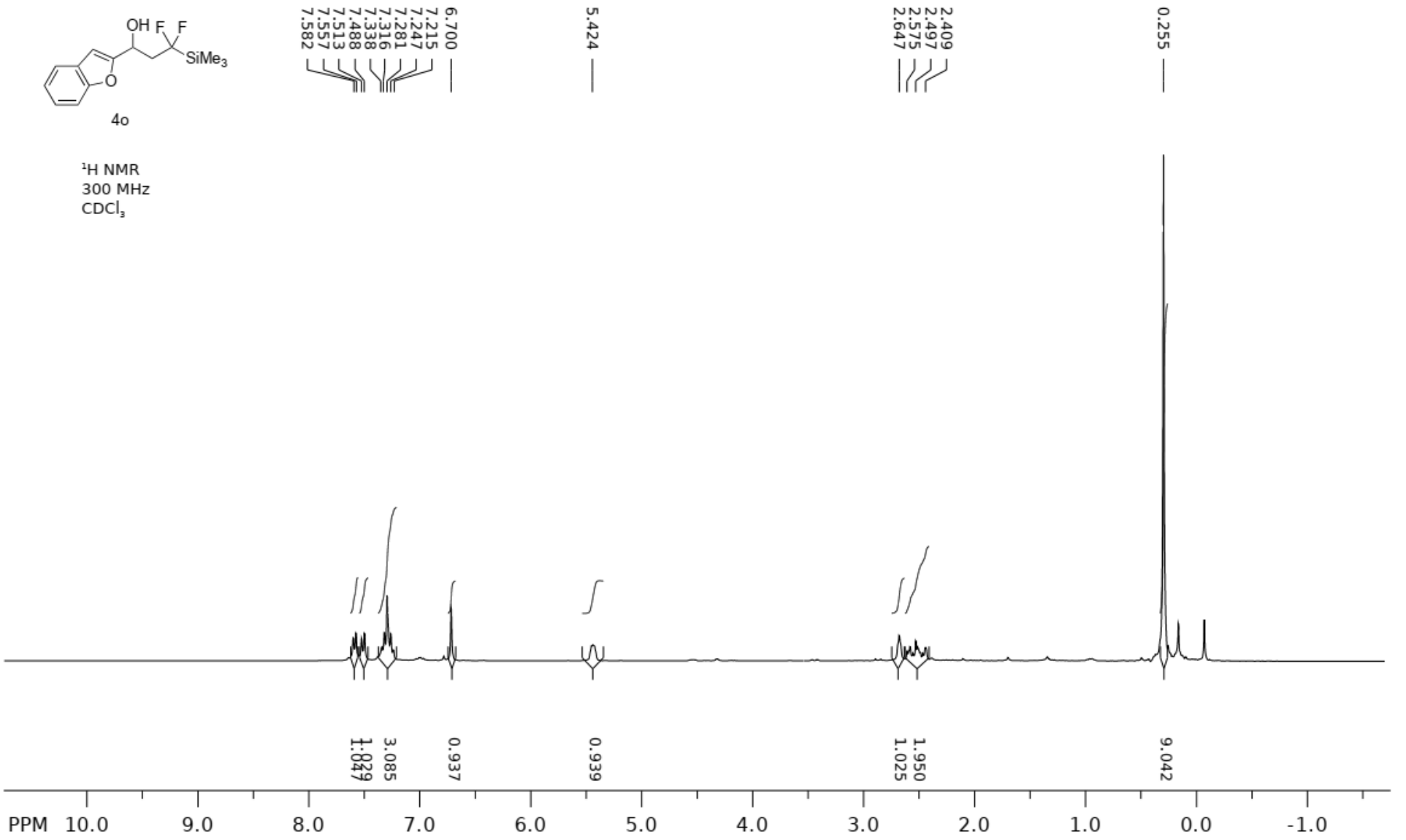

OH F F
SiMe3
S
4n
1H NMR
300 MHz
CDCl3
7.280
7.271
7.006
6.990
6.978
5.534
5.504
2.645
2.479
2.469
2.435
2.412
2.378
2.337
2.283
0.232
1.190
2.078
1.000
1.009
2.064
9.114
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

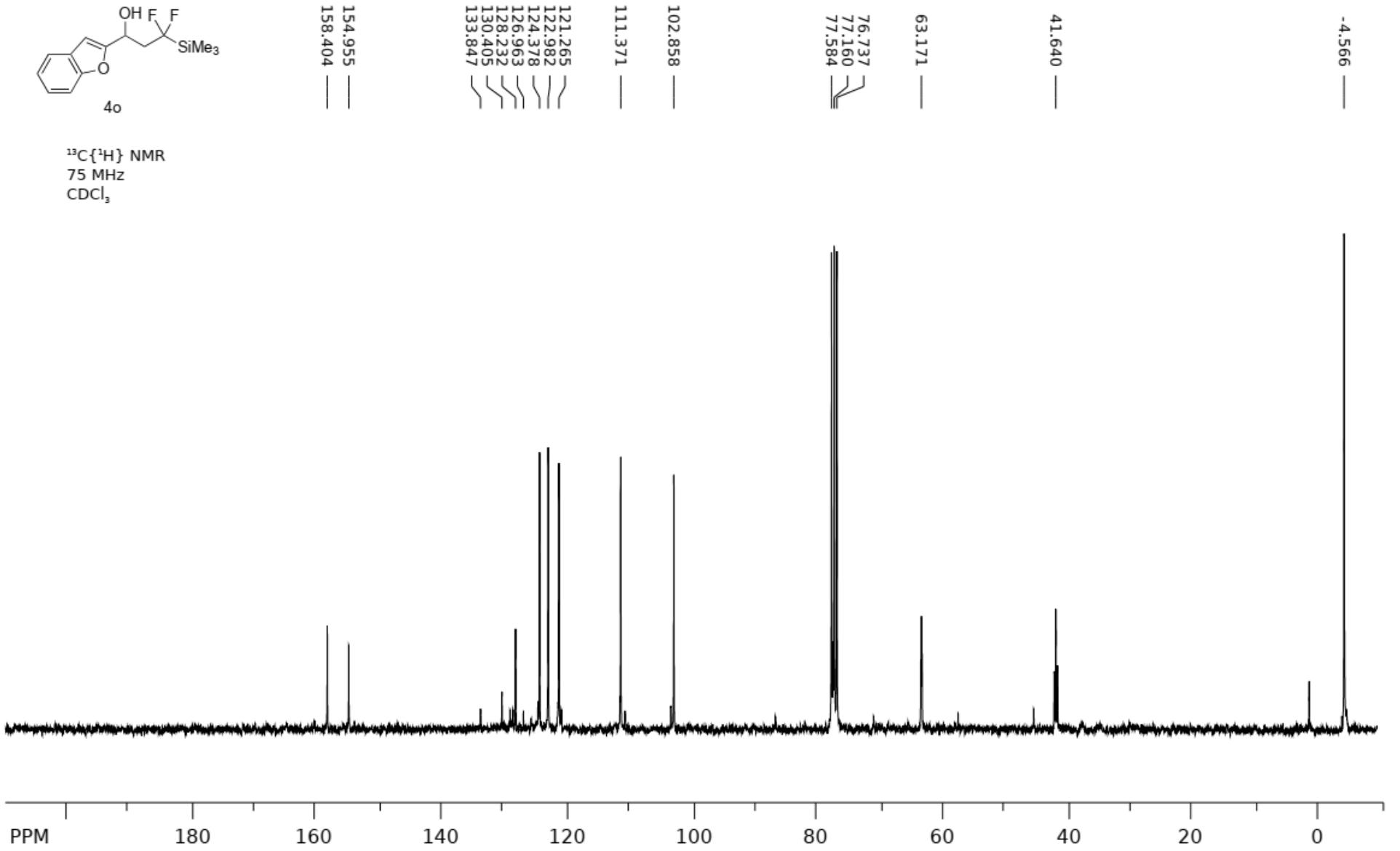

OH F F
SiMe3
S
4n
147.897
133.855
130.411
126.980
126.767
124.726
123.525
77.584
77.160
76.736
65.087
65.009
64.977
64.893
45.673
45.417
45.171
-4.529
-4.559
13C{1H} NMR
75 MHz
CDCl3
PPM
180
160
140
120
100
80
60
40
20
0

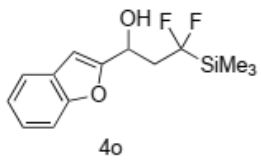


4n

^{19}F NMR
282 MHz
$CDCl_3$

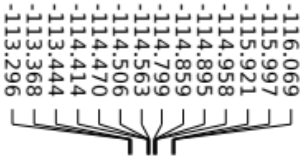

OH F F
SiMe3
O
4o
7.582
7.557
7.513
7.488
7.338
7.316
7.281
7.247
7.215
6.700
5.424
2.647
2.575
2.497
2.409
0.255
1H NMR
300 MHz
CDCl3
1.029
1.047
3.085
0.937
0.939
1.025
1.950
9.042
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

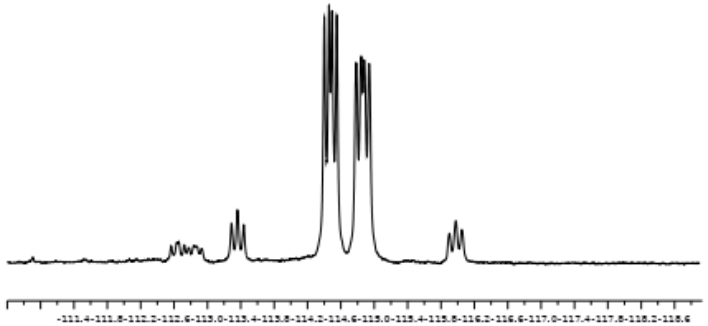

OH F F
SiMe3
O
4o
158.404
154.955
133.847
130.405
128.232
126.963
124.378
122.982
121.265
111.371
102.858
77.584
77.160
76.737
63.171
41.640
-4.566
13C{1H} NMR
75 MHz
CDCl3
PPM
180
160
140
120
100
80
60
40
20
0

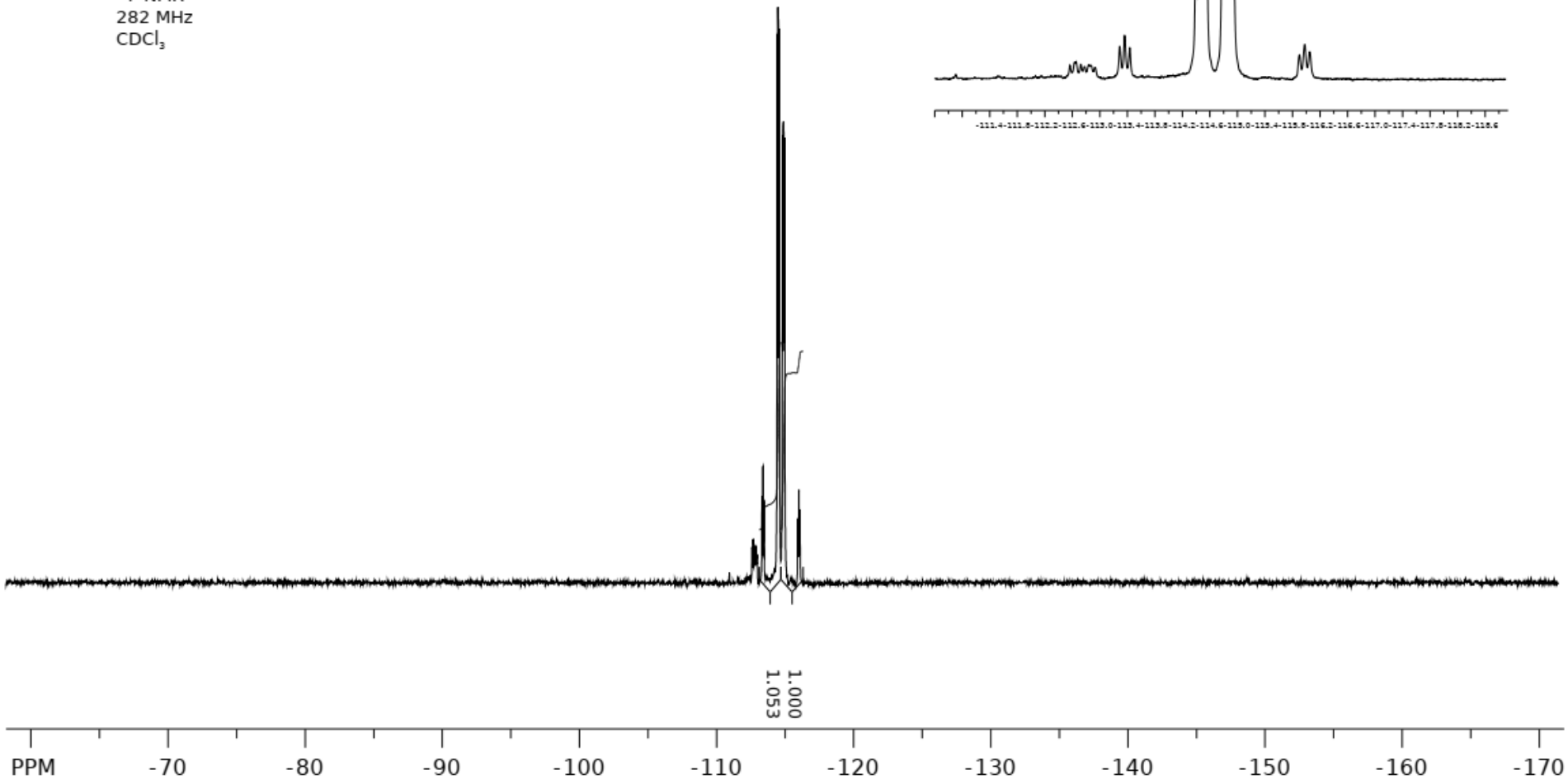


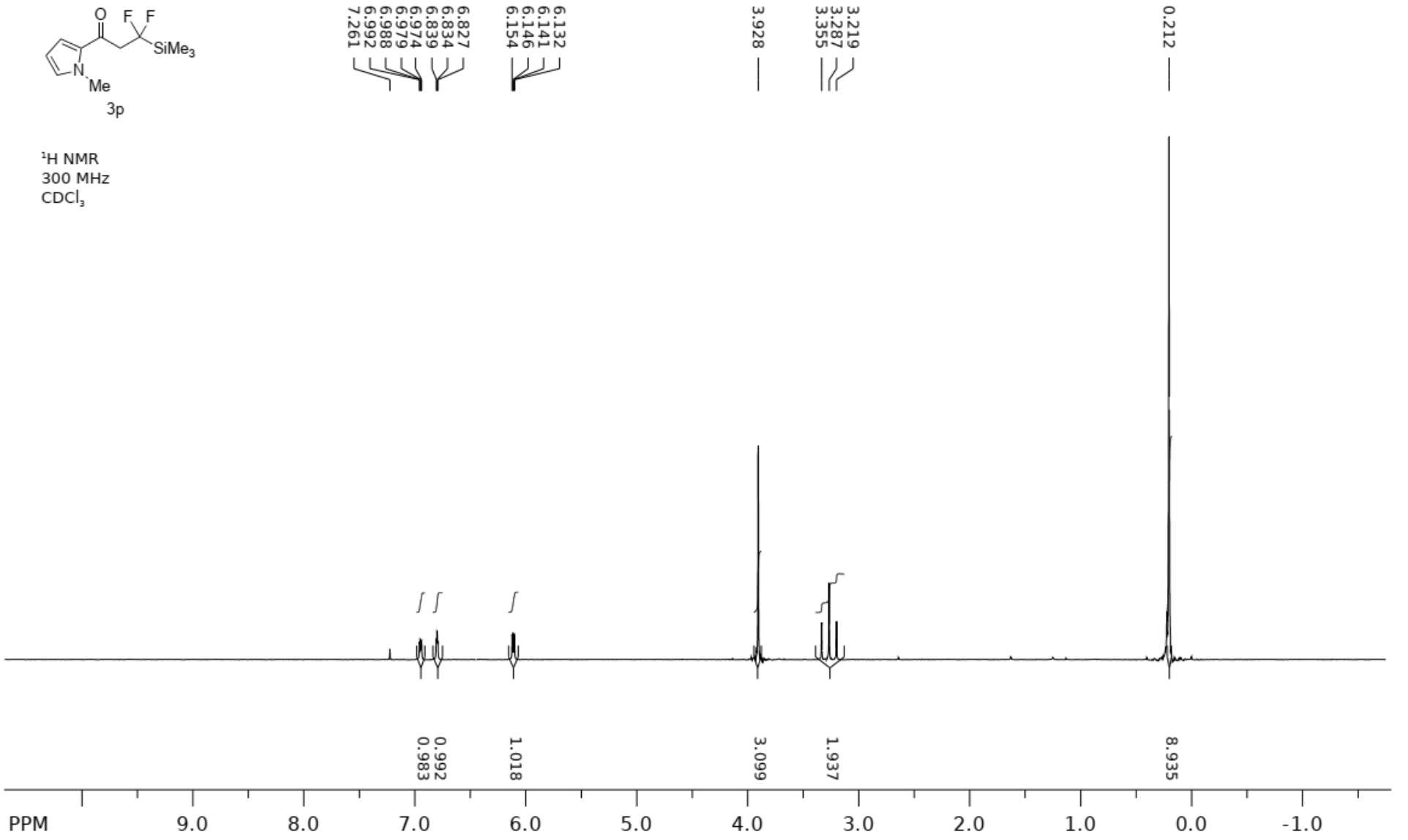
4o

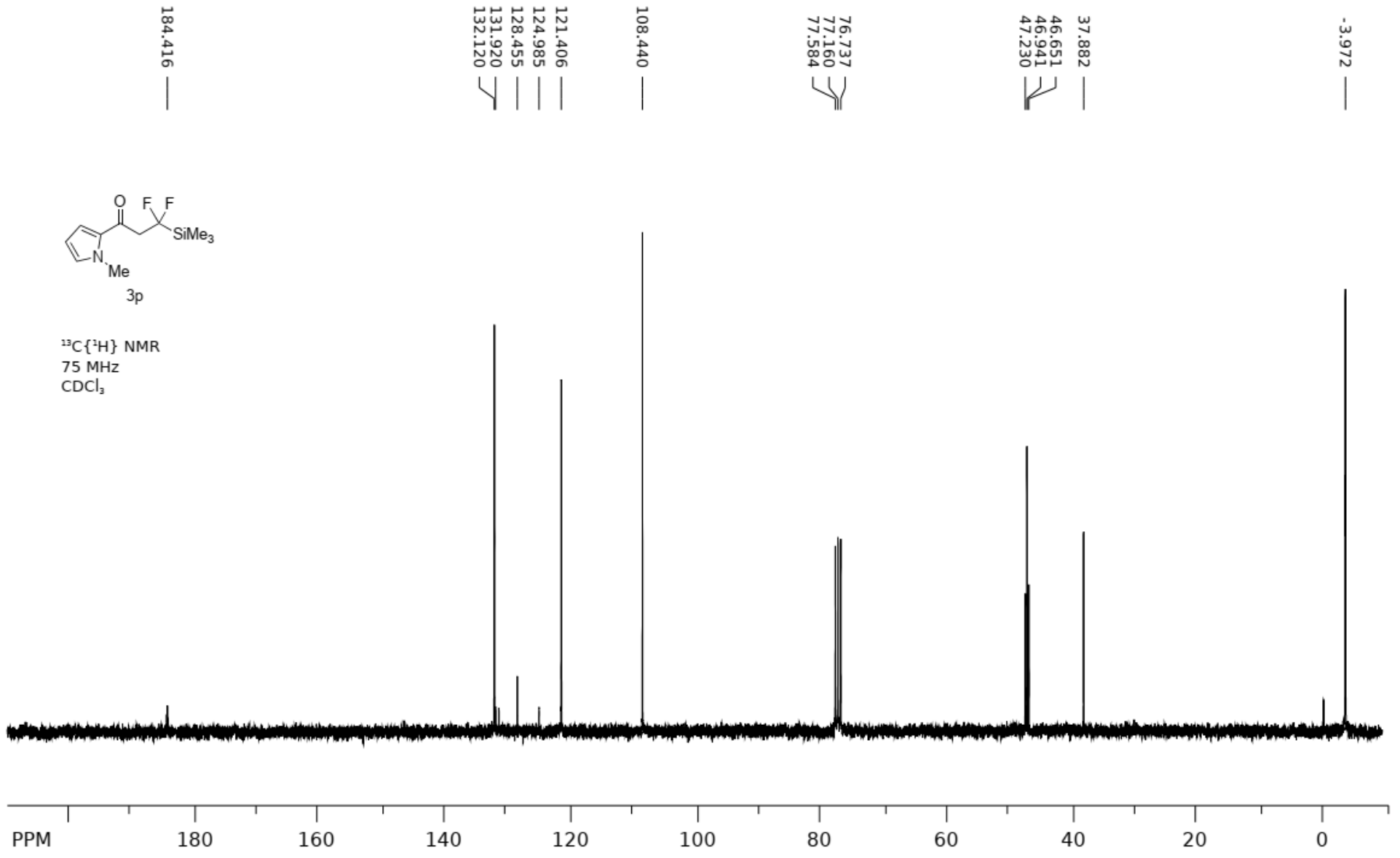
^{19}F NMR
282 MHz
$CDCl_3$

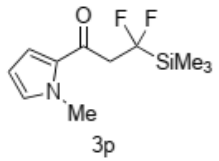







O
F
F
SiMe3
N
Me
3p
7.261
6.992
6.988
6.979
6.974
6.839
6.834
6.827
6.154
6.146
6.141
6.132
3.928
3.355
3.287
3.219
0.212
1H NMR
300 MHz
CDCl3
0.983
0.992
1.018
3.099
1.937
8.935
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


184.416
132.120
131.920
128.455
124.985
121.406
108.440
77.584
77.160
76.737
47.230
46.941
46.651
37.882
-3.972
O
F
F
SiMe3
N
Me
3p
13C{1H} NMR
75 MHz
CDCl3
PPM
180
160
140
120
100
80
60
40
20
0



3p

^{19}F NMR
282 MHz
$CDCl_3$

-107.731
-107.660
-107.589

-106.4 -106.6 -106.8 -107.0 -107.2 -107.4 -107.6 -107.8 -108.0 -108.2 -108.4 -108.6 -108.8 -109.0

PPM -55 -65 -75 -85 -95 -105 -115 -125 -135 -145 -155 -165